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Mr. W. L. FORSTER is home from Mexico.

Dr. E. PARSONS is home from South Africa.

Mr. STANLEY R. SAY has left Chile and is now in Mexico.

Mr. A. E. SOUTHERN is home from India.

Mr. Y. P. WILSON is home from Persia.

The Secretary will be glad to receive information as to the whereabouts of the following members:—J. M. BAILEY, D. H. GWINNER, L. B. HOLLOWAY, K. C. JOHNSON, I. C. LOW, E. C. MASTERSON, L. R. PHILLIPS, J. K. WALTON and S. S. WEBB-BOWEN.

The suggestion has been made that complete bound sets of the Journal should be available for sale to members of the Institution. Any member wishing to avail himself of this opportunity should communicate with the Secretary.

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In view of the proposed publication during the coming year of a second edition of "Standard Methods of Testing Petroleum and Its Products," it has been decided that the remaining copies of the first edition shall be made available at 3s. per copy on and after January 1, 1928.

TENTH ANNUAL DINNER.

The Tenth Annual Dinner of the Institution of Petroleum Technologists will be held at the Connaught Rooms, Kingsway, W.C. 2, on Wednesday, October 3rd, 1928. The arrangements are in the hands of Mr. Ashley Carter, Hon. Secretary of the Dinner Committee, to whom early application for tickets should be made. Tickets will be 12s. 6d. each, and members have the privilege of inviting guests. The seating will be arranged as in previous years, and will be carried out to meet members' wishes as far as possible.

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REPORTS ON THE PROGRESS OF NAPHTHOLOGY DURING 1927.

Chemistry.

By H. B. THOMPSON, M.Sc., Ph.D., F.I.C. (Member).

DURING the year under review a number of papers were published dealing with the origin of petroleum.

Ormandy, Craven, Heilbron and Chanson[1] review the work by Chapman and others on the hydrocarbon oil (squalene) present in the liver oils of the squalidæ sharks and its possible connection with the origin of petroleum is indicated. They describe the results of the berginisation of squalene whereby upwards of 60 per cent. of spirit and 30 per cent. of kerosene were obtained. The spirit contained unsaturated, aromatic and paraffin hydrocarbons. *d*-Pinene when berginised gave similar results to squalene, as was the case with some lignite oils, but the latter yielded some 20 per cent. of phenols.

Potonig[2] reviews the data and opinions of experts on the origin of petroleum, and the conclusions to be drawn from the presence of fossils.

Zelinski[3], by heating cholesterol with aluminium chloride, obtains a spirit distillate which on hydrogenation gave a saturated product consisting chiefly of cyclic hydrocarbons, of which several were identified. The higher boiling point fractions are optically active: sulphuric acid treatment almost removes this and their fluorescence; precisely similar observations have been made with natural petroleums.

Pratt[4] discusses the two theories of the origin of petroleum and quotes the researches of Tolman, which have shown the formation of oil to be a direct product of vital processes.

Fischer and Tropsch,[5] while synthesizing hydrocarbons from water gas when working at 10 to 15 atm. pressure and using an iron and copper catalyst impregnated with ½% potassium carbonate, obtained a quantity of a substance melting at 90 to 108° C. and of molecular weight 1000. Analysis corresponded to the formula $C_{70}H_{142}$. In the strongly exothermic reaction between carbon monoxide and hydrogen, the tendency is for the formation of compounds of very high molecular weight.

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[1] *Jour. Inst. Petr. Techn.*, 1927, **13**, 1.
[2] *Petroleum*, 1927. **23**, 395.
[3] Berichte, 1927, **60**, 1793.
[4] *Oil and Gas J.*, Sept. 29, 1927.
[5] *Berichte d D. Ch. Ges.*, June, 1927.

Fischer[6] in two papers on the synthesis of petroleum hydrocarbons, after reviewing recent work on the hydrogenation of coal, discusses recent progress in the synthesis of paraffin hydrocarbons by the hydrogenation of carbon monoxide under ordinary pressure. The difficulties of the purification of the water gas and regeneration of the catalyst have been overcome. The temperature of the cobalt or iron catalyst must be kept lower than that favourable to the production of methane, the necessary reaction rate being attained by suitable activation of the catalyst. The efficient production of benzine offers more difficulty than that of "Gasöl" or of the solid paraffins. The latter are produced when a strong base is added to the catalyst.

Otto[7] describes the formation from ethylene and its homologues of oils resembling closely in viscosity, flash point, &c., good lubricating oils prepared from petroleum fractions. In the presence of boron fluoride isobutylene polymerises vigorously to a thick colourless oil, propylene less readily and ethylene polymerises under pressure, the rate being increased by the presence of nickel. The small quantity of boron fluoride employed may be recovered and used repeatedly.

Butescue and Atanasin[8], by spectroscopic examination of a large number of samples of oil well gases showed that the helium content of these samples varied from 0·00006 to 0·0012 per cent.

Spilker[9], in discussing the composition and chemical constitution of lubricating oils and their synthesis, directs attention to the viscous, high molecular weight addition products obtained from bodies with double linkings. The viscosities (Engler) at 50° of additive and condensation products of benzene homologues were: from toluene-styrene, 0·4; xylene-styrene, 0·6; ψ-cumene-styrene, 1·2; toluene-allyl alcohol, 0·9; xylene-allyl alcohol, 2·2; ψ-cumene-allyl alcohol, 16·2.

The presence of methyl groups attached to aromatic rings greatly increases viscosity; normal hydrocarbon chains have little viscosity, but iso-compounds are highly viscous.

Reduction products from coal and coal tar by the Bergius process at lower temperatures and with nickel as a catalyst were examined.

Engler viscosities at 50° were determined for the hydrogenated products of accnaphthene, 0·5; phenanthrene, 0·6; anthracene, 0·4; fluoranthrene, 1·8; pyrene, 2·3; naphthafluorene, 3·1; and chrysene, 4·5.

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[6] *Fuel*, 1927, **6**, 89, and *Brennstoff Chem.*, 1927, **8**, 1.
[7] *Brennstoff Chem.*, 1927, **8**, 321.
[8] *Petroleum*, 1927, **23**, 391.
[9] *Petroleum*, 1927, **23**, 448.

Polyhydrides of chrysene have the characteristics of lubricants, but they are not identical with those from petroleum oils, the specific gravity being over 1·0 and the hydrogen content higher. The high molecular weight of substances derived from pitch favours the formation of highly viscous hydrogenation products.

Mabery[10], by a further series of brominations of various lubricating oils, confirms his original conclusion that these hydrocarbon mixtures do not contain olefine derivatives.

Haslam and Frölich[11] explain the mechanism of the oxidation of lubricating oils by the presumption that the hydrocarbons pass through the following stages of oxidation: Alcohols, aldehydes or ketones, and then to naphthenic or fatty acids or polymerise to asphaltic bodies. The effect of catalysts on the rate of oxidation was investigated and both negative and positive catalysts were found.

Much work has been published on the preparation of alcohols from petroleum derivatives.

Harris[12] reviews the general formation of hydroxy compounds from constituents of natural and still gases, and gives details of the preparation and uses of isopropyl alcohol. The conversion of propylene into alcohol is described by Davis.[13]

Kirkpatrick[14] gives the method used by the Sharples Corporation for the production of amyl alcohols from casing head gasoline. A fraction of b.p. 28-37° is chlorinated, and the amyl chloride hydrolysed with caustic soda in the presence of a catalyst. The alcohol fraction contains about 50 per cent. isoamyl alcohols, 25 per cent. n-amyl alcohol and 25 per cent. diethyl carbinol. The final product may be converted into acetate by acetylation with acetic and sulphuric acids in copper apparatus.

Koch and Burrell[15], after preparing amyl chloride from natural gasoline, convert this into the acetate by heating with sodium acetate in an autoclave to 400° F. in the presence of charcoal as a catalyst.

Patart[16] patents the preparation of higher alcohols from hydrogen and carbon monoxide at high temperatures and pressures in the presence of special catalysts. These are composed of alkali or alkaline earth salts of acidic metal oxides, such as those of manganese or vanadium or of the chromium-tungsten group, together with a methanol-forming oxide such as zinc oxide or pyrolusite.

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[10] *Jour. Am. Chem. Soc.*, 1927, **49**, 1116.
[11] *Ind. Eng. Chem.*, Feb., 1927.
[12] *Oil and Gas J.*, Jan., 1927.
[13] E.P. 249,834, Jan. 13, 1927.
[14] *Chem. and Met. Eng.*, 1927, **34**, 276.
[15] *Ind. Eng. Chem.*, 1927, **19**, 442, and *Oil and Gas J.*, April, 1927.
[16] E.P. 250,563 and 252,361, Aug., 1927.

The gas mixture, after circulation over the catalyst, is cooled under pressure to condense the alcohols and water formed. The mixed alcohols are fractionated about 60 per cent., consisting of propyl, butyl and anyl alcohols.

If the reacting gases are not freed from sulphur, catalysts of the type described above become poisoned after some 200 hours' activity. They can be regenerated by calcination in an open crucible or by slow circulation through an oxidising flame. The S.A. d'Explosifs et Produits Chemiques[17] separate pentane amylenes and butylenes from cracked gases by successive operations of compression and cooling.

From the residue propylene is removed by sulphuric acid, and the remaining gases are chlorinated to monochlor derivatives. All the products are chlorinated and converted into alcohols.

By subjecting ethylene to a silent discharge at a potential of 12,000 volts Demjanov and Prianishnikov[18] obtained a mobile yellow oil of specific gravity ·836 and average molecular weight 215, consisting of unsaturated hydrocarbons from C_6H_{12} upwards, together with saturated compounds. Isobutylene gave a product containing chiefly the hydrocarbons C_8H_{16} and $C_{12}H_{24}$.

Taylor[19] has succeeded in using diethyl sulphate in place of dimethyl sulphate, with its very marked toxic action as a means of differentiating between paraffinoid and naphthenic and unsaturated and aromatic hydrocarbons.

Appleby and Carter[20] have patented improvements in the manufacture of solid sodium hypochlorite preparations.

A strong solution of the hypochlorite is mixed with a partially or wholly dehydrated salt of sufficiently alkaline character such as sodium metaborate. Trisodium phosphate or disodium phosphate and caustic soda may also be used.

Lorand[21] has studied the action of sulphur monochloride on individual hydrocarbons and finds that there is a marked difference in the action on saturated and unsaturated hydrocarbons.

Gordon and Marshall,[22] by means of a Hele Shaw stream line filter, have isolated waxes from untopped Persian crude oil. Edge filtration appears to establish conditions in which a protective colloid is unable to function and an apparently colloidal material was actually isolated. The removal by solvents of this material renders possible the crystallisation of the wax, and in one case rendered possible the coagulation of the remainder by cooling.

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[17] E.P. 251,652, Aug., 1927.
[18] *Jour. Russ. Phys. Chem. Soc.*, 1926, **58**, 462.
[19] *Ind. Eng. Chem.*, *Jan.*, 1927.
[20] E.P. 274,197 and 274,198, 1927.
[21] *J. Ind. Eng. Chem.*, June, 1927.
[22] *J. Soc. Chem. Ind.*, July, 1927.

Hoover, Dorcas, Langley and Mickelson[23] give details of the catalytic preparation of unsaturated hydrocarbons from carbon monoxide and hydrogen.

Data concerning sixty-four catalysts are given. One of the most efficient was nickel-palladium deposited on aluminium. Copper and cobalt were the only two single substances to catalyse the reaction, and apart from these an interface of two metals appears essential.

The presence of 1 per cent. of oxygen seemed to favour the production of hydrocarbons, whereas carbon dioxide and water in any appreciable quantity seriously interfered with it.

Patart[24] synthesizes methanol and liquid hydrocarbons by circulating a mixture of approximately equal volumes of coal gas and water gas over a zinc oxide-chromium oxide catalyst at 150-200 atm. and 300° C. for eight hours.

It is claimed that the hydrocarbons are formed from the ethylene, while the methanol is produced by the hydrogenation of the acids of carbon either present or formed by the incomplete combustion of the methane.

Folliet[25] converts methane into higher hydrocarbons by subjecting the methane to a gradual heating, followed by a sudden cooling when the highest temperature has been reached, the products of reaction being kept under a vacuum until completely cooled.

Morris and Reyerson[26] have studied the hydrogenation of ethylene under different conditions by silica gels metallised with platinum palladium and copper. Under standard conditions the palladised and platinised gels reached their maximum efficiency at 60° C., while the copperised gel was most efficient at 240° C.

Smith[27] has theoretically investigated the equilibrium conditions in the formation of hydrocarbons and alcohols from water gas.

In a contribution to the study of Berginisation, Waterman and Perquin[28] deal with the differences which obtain between the spirits produced by cracking and by Berginisation.

Further work[29] on the nature of the liquid reaction products of the Berginisation of paraffin wax contains a summary of the refractive indices and dispersive powers of several hydrocarbons of different groups. Different examples are quoted to show the use of refraction values, (McIlhmey) bromine values, and (Victor Meyer and Rast) molecular weight determinations in investigations of the purity of hydrocarbons.

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[23] *J. Amer. Chem. Soc.*, **49** (iii.), 796.
[24] E.P. 247,932, April 28, 1927.
[25] E.P. 271,767, June 2, 1927.
[26] *J. Phy. Chem.*, 1927, **31**, 1220.
[27] *Ind. Eng. Chem.*, 1927, **19**, 801.
[28] *Bull. de la Soc. de Chem. Indus.*
[29] *J. Inst. Petr. Techn.*, 1927, **13**, 413.

Brame and Hunter[30] have carried out an extended investigation on the composition of cracked distillates and the following bodies were identified:

Paraffins and *isoparaffins*—hexane heptane and the iso hexanes, dimethyl-ethyl-methane and di-iso propyl. The presence of pentane, isopentane and iso-heptanes was also indicated.

Naphthenes are present to about the same extent as the paraffins. Methyl-pentamethylene, hexamethylene, dimethyl-pentamethylene and methyl-hexamethylene were isolated, but pentamethylene could not be detected.

Olefines are the predominating unsaturated hydrocarbons in the lower boiling fractions. Those of the type $RCH=CH_2$ appear to be absent; 3 and 2-methyl pentane and 4 and 5-methyl hexene are probably present.

Di-olefines.—Indications of the presence of these compounds were obtained in the lighter fractions with definite evidence of the hydrocarbon piperylene.

Cyclic olefines predominate among the unsaturated compounds boiling from 90-120° C.

Aromatics.—Small percentages of hydrocarbons of this class are present in the spirit.

Lewis[31] publishes results of investigations on the low temperature oxidation of hydrocarbons and discusses the bearing of these on the theory of anti-detonation.

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[30] *J. Inst. Petr. Techn.*, 1927, **13**, 815.
[31] *J. Chem. Soc.*, July, 1927, 1555.

Refining and Refineries.

By J. McConnell Sanders, F.I.C., F.C.S. (Member).

General.

Overproduction of crude oil was the predominant feature of the world's petroleum activities during the year 1927. The previous year had ended with the creation of a record in total production, but the period under review was characterized by still further activity.

In the United States it is calculated that the production was raised to nearly 7 per cent. over actual requirements, and the result of this surplus of 7 barrels in every 100 produced was far reaching in its economic effects.

According to one authority[1] the market value of oil company's stocks was depreciated by $1,000,000,000, or put in another way, the investor in the industry had to pay $14 a barrel more than the price received for the oil.

The 1926 record in production created by the United States was broken in 1927, when nearly 906,000,000 barrels was taken out of the ground, and it is interesting to note that about 86 per cent. of this was light crude of specific gravity 0·909 or below, as compared with about 82 per cent. for the previous year.

Russia showed a noteworthy increase in production, rising from third to second place in order of productivity, and this is the more remarkable when it is considered that mechanical equipment in the oil fields of that country, and facilities for transportation, are far from adequate, while, as pointed out by J. H. Nelson in a paper read before the American Institute of Mining and Metallurgical Engineers,[2] improvement in these conditions has been restricted by the failure to obtain credits from foreign capitalists.

In a previous review[3] the author predicted that Mexico's position among the world's producers would probably be usurped by one of its neighbours in the south, and in actual fact the prediction was verified in 1927 when Venezuela and Mexico reversed their positions in the order of productivity.

The approximate yield from the Mexican fields was 64,200,000 barrels, it being computed that 552 wells were completed, of which 177 were producers, as against 863 completed in 1926 with 290 producers.

Venezuela only produced about 258,000 barrels more than Mexico during the year, but could certainly have increased this figure if more tank ships had been available for removing the oil to refineries in other countries.

The relative position of the world's producers during the year under review is shown in the following table :—

	Per cent.
United States	72·23
Russia	5·77
Venezuela	5·14
Mexico	5·12
Persia	2·93
Rumania	2·08
Colombia	1·16
All other countries	5·57
	100·00

[1] *Oil and Gas J.*, **26**, 27, 157.
[2] New York Meeting, Feb. 20, 1928.
[3] *J. Inst. Petr. Techn.*, **13**, 63, 517-530.

It is worthy of note that among those minor producers which are together responsible for 5·57 per cent. of the total production, the Argentine and Peru now figure as supplying about 18 million barrels in the year, and this fact, together with the growing activity of Venezuela and Colombia, plainly indicates the southward tendency of oil seekers in the American Continent.

Simultaneously with the oil developments in Latin-America has appeared the tendency to imitate the Mexican policy of governmental control of the industry, but as pointed out by several writers in the American press, this tendency is not confined to America, for the nationalization of the sources of crude supply and the monopolistic control of the sale and distribution of the products have featured in recent legislative enactments by many European countries.

Undoubtedly the United States regards this nationalistic tendency in other countries as likely seriously to influence its own export trade, but the overproduction in both 1926 and 1927 and the consequent lowering of prices for all classes of petroleum products, have had a counter-balancing effect, and the causes mentioned have also restricted to a considerable extent the incentive to discover substitutes for these products.

Nevertheless, the efforts in Germany to develop an "oil-from-coal" industry indicate clearly that this country, like several others which do not count large supplies of petroleum among their national possessions, is seeking eventual independence from foreign sources of supply.,

Italy, Spain and France are among those which introduced special legislative measures in 1927 in order to assure governmental control of petroleum supplies, while Poland established a new Cartel having in view the same object.

A factor of no small importance is the continually increasing use of motor cars. According to one authority[4] the number of automobiles in use up to July, 1927, amounted to 25,202,000, inclusive of motor trucks, and these were distibuted as follows :—

United States	22,137,000
United Kingdom	1,023,000
France	891,000
Canada	828,000
Germany	323,000

It is notewothy also that overproduction and low prices have not restricted the efforts of engine designers continually to improve the efficiency of their machines. In Great Britain the onerous horse-power tax has naturally provided good and sufficient reason

[4] Commerce Reports, July 11, 1927.

for the public demand for highly efficient engines with low fuel consumption, but it is significant also that during the year under review the generality of automobile manufacturers in the United States raised the compression ratios of their engines as compared with previous practice, while the "H.U.C. value" of motor spirits became a "talking point" amongst salesmen instead of being a technical hieroglyphic with a meaning known only to the initiated.

Refineries.—According to C. O. Wilson[5] the year 1927 showed an increasing trend in the United States towards the adoption of fewer and larger operating units. This author points out that this tendency has been evident for the past four years, the maximum number of refineries being 584 in 1925 of which 385 were operating. In 1927 the existing refineries totalled 462 with 328 in operation, and yet the daily refining capacity in the latter year was 284,375 barrels more than in the former.

It is also pointed out that many of the plants shut down were small skimming and topping plants which could not be operated in competition with installations owning modern equipment.

Another interesting fact is the relatively small increase in the number of new cracking plants, although the cracking capacities of the existing units were rated higher. This is attributed in part to the unfavourable market conditions owing to overproduction, but it is also reflected in the very considerable improvements made in the design and efficiency of the equipment.

According to government reports some 101,224,000 barrels of cracked gasoline were produced, showing an increase of about 7 per cent. over the 1926 production, and this increased yield was produced with fewer cracking units.

Not only as regards cracking plants has improved design been responsible for the increased refining capacity of the operative installations, in many cases the substitution of old cylindrical stills by modern tubular equipment has been a definite policy with many companies, and there was a marked increase in the use of fractionating towers, leading to better recovery of light fractions and larger crude throughputs.

The preliminary report of the United States Government for the year 1927 shows that the crude oil run to stills totalled 828,514,000 barrels, of which 48,701,000 was from foreign sources. The recovery of gasoline amounted to 330,667,000 barrels, or nearly 40 per cent., as compared with 38·5 per cent. in 1926.

This progressive improvement in the United States refining industry has not prevented other countries from improving their

[5] *Oil and Gas J.*, **26**, 27, 157.

facilities. In the Argentine for instance the operation of the Government Refinery at La Plata resulted in a decided decrease in that country's importations of American gasoline, while in Great Britain the importations of crude oil from Persia, Venezuela, Mexico and Colombia, to be refined in British refineries, has also shown a marked tendency to increase, with consequent diminution in the import of refined products from the United States.

In Canada considerable increase in refining capacity was reported, while in Venezuela similar progress took place. On the island of Aruba, Dutch West Indies, a large refinery was constructed by the Arend Petroleum Company, one of the subsidiaries of the Royal Dutch Group, while on the same island or in Venezuela, it is reported that an American Company is also contemplating the establishment of a refinery.

Refinery Plant and Equipment.—The substitution of the old form of under-fired shell stills by tubular heating elements connected to some form of separator continued to gain ground in refinery practice generally. In the United States one or two refineries favoured the locomotive type of cylindrical still instead when modernising their equipment. Such stills were provided with as many as 20 four-inch diameter tubular flues, and the setting of the still was so arranged that the hot combustion gases made a double pass, travelling at first underneath the shell to the back of the setting and then returning through the tubes to the firing end of the still before entering the stack.

In the case of tubular heaters considerable attention was devoted by designers to the problems involved when dealing with high temperature distillations. The transition of the pipe still from an apparatus for simply topping to a complete substitute for the cylindrical reducing or lubricating still, may now be taken as an accomplished fact, and marks an important advance in the evolution of modern distillation apparatus.

One of the causes leading to improvements in modern furnace design was the gradual abandoning of the old theory that surfaces for heating oil should not be exposed to directly radiated furnace heat.

In a paper read before the American Institute of Mining and Metallurgical Engineers, A. E. Nash shows that in ordinary types of furnace design it is the combined effects of radiant and convection heat which would probably cause trouble. With high gas temperatures the furnace settings become incandescent and might radiate heat at a temperature as high as 2,400°F., assuming an oil temperature of 800° F., the combined rate of heat transfer by radiation and convection might approximate 110,000 B.Th.U. per square

foot of exposed surface, which might be more than either the metal or the oil could stand.

This author also points out that the use of Dutch ovens, bridge walls and arches does not prove a satisfactory preventative for local overheating, and therefore the former practice was to purposely supply excess air in order to keep the temperature down, this naturally leading to low fuel efficiencies. He maintains that when properly applied, radiant heat has several advantages, and actually results in economy of fuel.

The present tendency in furnace design is exemplified in the patent granted to J. Primrose,[6] who divides the tube heater into two compartments by means of a bridge wall. One of these compartments is the combustion chamber proper, the other is a heating chamber. A horizontal row of tubes encased in iron blocks are placed close to the roof of the furnace, the blocks serving to absorb the radiant heat and to protect the tubes.

Banks of tubes are also placed in the heating chamber, and these tubes may be corrugated or "gilled" to increase the heating surface.

The oil is fed into the lower bank of tubes counter current to the flow of furnace gases, and then to the tubes in the roof of the combustion chamber and from thence to the upper bank of tubes in the heating chamber, where its direction of flow is parallel to that of the furnace gases.

In the last stage of its travel the temperature difference between the furnace gases and oil tends to diminish.

Tubular heaters of the type described are being installed in increasing numbers in the United States, and combined with suitable fractionating towers are proving themselves capable of performances scarcely thought possible a few years ago. In fact, for some types of crude oil, such a combination may entirely replace the separate benches of crude and re-run stills which formerly constituted a complete refinery. It is by no means unusual for such a plant to yield 95 per cent. of its throughput as distillate, the latter including gasoline, kerosine, gas oil, pressable wax distillate and heavy lubricating stock.

A method of securing an even distribution of heat was patented by H. E. Gilbert,[7] who provides a wall between the furnace chamber and the still whether of the shell or tubular type. This wall varies in thickness and consequently in conducting power, being thickest at the point where the flame from the burner enters, and gradually thinning down towards the end of the flame, where it is perforated by several holes.

[6] U.S.P. 1,626,874.
[7] U.S.P. 1,621,319.

A somewhat novel method of heating a still of the vertical type is the subject of a patent by G. D. White,[8] who proposes to apply heat to the middle zone of the shell only, leaving the bottom and top of the still unheated.

By this means it is claimed that carbon and heavy residuum settle to the bottom without being adherent, and may from thence be drawn off.

F. T. Manley[9] goes to the other extreme in patenting a form of still in which practically the whole of the periphery is heated, both the liquid and vapour space, the latter however being protected by suitable lagging.

The evaporation of liquids by means of heat applied to their surfaces has been applied previously for concentrating purposes, notably in the case of sulphuric acid. J. Jakowsky[10] has, however, obtained a patent for a method in which bituminous material is distilled by exposing only its upper surface to a source of radiant heat, the mass being progressively stirred.

An improvement in the method of heating a still by side firing is the subject of a patent by R. A. Porterfield.[11] According to this a cylindrical still is supported by a setting which embodies a number of walls transverse to the length of the still. These walls provide points of support to the still bottom if substantial sagging should take place, while between the walls are installed separate furnaces by means of which heat may be applied and evenly distributed along the bottom of the still.

A method of improving the circulation of oil inside a still is provided by a patent granted to C. W. Stratford,[12] according to which a pump is installed inside the still which draws oil from a point below the surface and discharges it at high pressure through a manifold against the heated inner surface of the shell. The method also embodies the preheating of the incoming charge of oil by causing it to flow down inclined plates inside the still, these being covered with netting which is said to cause a rippling movement to the oil and the latter being spread in a thin film is preheated before mixing with the main body of oil.

The recirculation of hot flue gases from still furnaces was incorporated in the design of several new plants erected during the last few years, and patents continue to appear covering this method of economising heat.

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[8] U.S.P. 1,621,298.
[9] U.S.P. 1,640,202.
[10] U.S.P. 1,622,722.
[11] U.S.P. 1,647,664.
[12] E.P. 280,727.

J. E. Bell[13] patented a distilling apparatus in which hot furnace gases pass through tubes immersed in the oil and then return by two central flues located in the still and thence pass to the stack. By-passes are made between the firebox and the flue adjacent to the stack and air passages are provided in the central flues, the air entering at the firebox end of the still and being discharged at the other.

In another patent[14] claim is made for a system wherein hot gases which have previously passed over a heating surface of the still are mixed with products of combustion before again passing over a heating surface, and air, preheated by heat exchange with waste combustion gases, is supplied to the firebox.

The preparation of motor fuel from coal is usually regarded as a separate branch of technology from that connected with petroleum, in fact it may eventually prove a serious competitor to the latter. In a process invented by W. M. Duncan[15] the rival industries are called upon to unite their forces in providing a means for distilling liquid and solid hydrocarbons at the same time. In the apparatus described a grid arranged inside a still supports a mass of coal, which may be submerged in the liquid hydrocarbon. The vapours from the liquid are conducted to a vapour line in which are incorporated a pair of chambers suitably lagged, the upper parts of which are united to a reflux condenser from which a connection is made to a final condenser.

A reflux line is provided from the reflux condenser to the still, and each of the chambers in the vapour line contains a charge of bituminous coal or other solid hydrocarbon, supported on a grid through which the vapours may pass. Both liquid and solid hydrocarbons are maintained at a temperature sufficient to release their volatile components, which are then condensed together. The object of the double chamber is to permit recharging of one of them without interrupting the distillation, and suitable valves are provided to allow the vapours to be diverted through one or other of them, while after the introduction of a fresh charge, air may be expelled by the introduction of steam. It is claimed for this process that a new motor fuel is produced without over-heating the coal, while the residue from the latter is a smokeless fuel.

Controlled fractionation is a feature highly characteristic of the present trend in the design of modern distilling plants. In the now familiar "bubble tower" thermostatic devices are sometimes incorporated in order to control reflux temperatures, while the fractionating towers themselves are often provided with special

[13] U.S.P. 1,613,306.
[14] U.S.P. 1,623,773.
[15] U.S.P. 1,654,797.

devices which permit very close control of the qualities of the fractions. Quite a number of special dephlegmating devices have also been brought out during the year under review, amongst which may be mentioned the arrangement patented by D. Pyzel,[16] according to which the vapours coming from a still pass into a dephlegmator down which flows cold condensate from a re-run still which acts as a cooling and absorbing agent.

Hot condensate from the dephlegmator is returned to the re-run still which is composed of two end chambers connected by pipes, which run through a central chamber. The major portion of the condensate enters one end chamber and flows through the pipes to the other end chamber from which it is withdrawn, cooled and returned to the dephlegmator. The minor portion is admitted to the central chamber and is heated by the hot condensate passing through the central pipes, and also by the admission of steam, and is thus distilled, the light distillate being drawn off. It is claimed that a fraction can be withdrawn from the central chamber which will boil between definite temperature limits.

A dephlegmator of variable capacity is described by J. D. Seguy[17] which follows the conventional design in having a cylindrical shell with perforated baffle plates, but incorporates an arrangement of separate draw-off outlets at varying heights up the sides of the shell, these being connected to a pump through a common manifold. There are also a series of vapour inlets at corresponding positions up the sides of the shell of the dephlegmator, so that vapours can be introduced just above the liquid level. Spray inlets for raw oil and condensate from escaping vapours are also provided, as well as a liquid draw off at the bottom.

In order to rapidly separate drops of condensate from a mixture of hydrocarbon vapours the latter are sometimes allowed to flow tangentially into a cylindrical chamber so as to produce a whirling movement and throw off the heavier liquid to the periphery of the chamber by centrifugal force, a modification of this idea is incorporated in the patent of J. A. Milliff,[18] who first cools the vapours to a pre-determined temperature, then causes them to expand suddenly and rotate at an accelerating speed to separate the condensate formed by the cooling. The collected condensate is in communication with the vapour mixture.

The use of molten metals for the transfer of heat to oil is an old idea in the history of refining, although never utilized to any great extent by refiners. C. Field took out a patent in 1922 for a

[16] U.S.P. 1,622,737.
[17] U.S.P. 1,623,136.
[18] U.S.P. 1,620,163.

method of heating oil to high temperatures by means of mercury vapour, and this patent[19] described a system whereby the mercury was vaporized in a separate boiler and the vapour passed through a superheating coil into a jacket surrounding the oil container. The mercury vapour condensed in the jacket and was returned to the boiler. In 1927 this inventor was granted patents[20 21 22 23] covering several modifications and improvements, such as the use of the mercury in the boiler as a resistance so as to allow it to be heated electrically, the transfer of the heat from mercury to oil by means of internal tubes, and arrangements for more efficient condensation of the mercury vapour.

The corrosion problem has occupied a promient position among refinery technologists during the year, and numerous writers in the technical press have contributed their ideas regarding its solution. The greater number of these have undoubtedly been stimulated by the Symposium on corrosion instigated by American Petroleum Institute in December, 1926, but the problem is still a very serious one to refiners who have to deal with the sulphurous crudes from Texas, while Mexican refiners have for long past considered it as a normal factor in their operations.

An article by Egloff and Morrell[24] reviews the use of reagents for controlling corrosion and the quantities usually employed. It draws attention also to the fact that secondary corrosion and embrittlement of the metal of stills is likely to be caused by the use of caustic alkalis, and states that lime is used to overcome such effect with marked success.

M. Freund[25] concludes that the presence of chlorides in the water which accompanies the oil, and the production of carbon dioxide by partial oxidation of unsaturated hydrocarbons are both causes of corrosion in a crude distillation plant. He affirms that the oxidation is due to air, trapped in the steam or to leakage. He advocates the use of air-free water in the steam boilers in addition to the use of lime or dilute alkali in the distilling system.

Mitchell[26] writes with regard to the use of special alloys for resisting corrosion and states that no definite alloy resistant to all corrosive substances is at present known. He presents a theory to account for the resistance to corrosion of metals and alloys, and gives a list of the most important ones.

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[19] U.S.P. 1,403,471.
[20] U.S.P. 1,619,660.
[21] U.S.P. 1,619,661.
[22] U.S.P. 1,619,662.
[23] U.S.P. 1,619,663.
[24] *Oil and Gas J.*, 1927, 26, 29.
[25] *Chem. Zeit.*, 1927, 51, 528.
[26] *Ind. and Eng. Chem.*, Nov., 1927.

Treating Methods.—Probably the most characteristic feature of the year's progress in treating methods generally is the more general use of some form of siliceous clay as an adjunct to or instead of sulphuric acid. One reason for this is the extended manufacture of cracked motor spirit, and the well-known fact that the removal of deleterious sulphur compounds and gum-forming components cannot be achieved by sulphuric acid treatment without occasioning great loss of material.

While Fullers earth or "Floridin" still represent the most used type of clay for refining purposes a great number of natural, or artificially treated and activated earths have appeared on the market during the year.

An article by H. L. Kauffman[27] describes experiments made with clays of the bentonite type from Arizona by treating them with 50 per cent. by weight of 66° B. acid, adding water to reduce the concentration to 20 per cent. and then digesting the mixture for five hours at 200° F. After washing the pulp four times with water at 180° F., the pulp is then stated to be 5·7 times as efficient as fuller's earth for treating cylinder stock in the acid state, and 6 times more than that material in the case of an asphaltic base lubricating distillate, while with neutral motor oils its efficiency was 10 times more.

I. A. Clark secured a patent[28] in 1925 covering the treatment of clay with water to remove impurities, the plastic mixture being added to the oil and heat applied to drive off the water. Together with H. L. Kauffman this inventor patented a somewhat similar process,[29] according to which the clay is mixed with from 30 to 500 per cent. of water by weight, and the mixture pumped to an agitator, where it is mixed with the oil which has usually been previously acid treated. The mixture is then passed through heating coils, where its temperature is allowed to rise to a little below the boiling point of the oil and discharged into a separator in which steam and oil vapours escape as distillates and oil falls to the bottom. Steam is injected into the bottom of the separator until the oil has cooled to about 110°, whereupon it is pumped to a settling tank and the clay subsequently removed by filtration or by centrifugal separation.

The use of clay for treating gasoline in the vapour phase has continued to receive attention from refiners, in one American refinery 8,000 barrels of spirit are treated daily by this means, and the Barnsdall Refineries Co. have introduced an improvement

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[27] *The Refiner*, Aug., 1927.
[28] U.S.P. 1,533,060.
[29] U.S.P. 1,636,938.

in connection with the use of Gray towers for this purpose, by flushing the exhausted clay with gasoline passed backwards through the system in order to remove polymerised compounds which have accumulated therein.

The use of clay in the manufacture of lubricating oils is rapidly becoming more generalised. In the so-called "dry process" it is used to neutralise a lubricating oil which has been treated with acid and the major part of the sludge removed by settling. It thus takes the place of the usual water wash and alkali treatment. In the "contact process" the clay is used for bleaching or improving the colour of the oil, and may be applied to an acid treated, but still unneutralised or washed oil, or to a neutral oil. It may also be applied to an oil after it has been re-treated with acid, using an amount of the latter sufficient to give it a colour which could only be procured by the more expensive process of percolation through granulated earth.

The contact process therefore combines the functions of the neutralising or dry process, and the decolourising action, and in both processes entails the thorough mixing of the oil with finely divided earth which is subsequently removed by filter pressing. It is generally found that the best method of mixing the oil and earth, is by means of a centrifugal pump, which may be connected in series with a heater for the oil-earth mixture. According to Bierce[30] the use of open steam is advantageous in preventing oxidation of the oil, but it should not be applied until the temperature of the oil has risen high enough to prevent the condensation of droplets which inhibit the action of the clay.

In refining by sulphuric acid, neither neutralisation nor washing are sufficient to completely remove acidic compounds. E. B. Phillips and J. G. Stafford[31] have patented a process for refining which is more particularly applicable to those acid treated oils which have to be re-run. It is pointed out that the acidic compounds decompose on distillation and compounds are formed with the unsaturated hydrocarbons present, causing discolouration.

The method described consists in distilling the oils under a reflux tower in which the vapours are brought in contact with an alkali during a prolonged period. The alkali may be applied as an aqueous solution or suspension or in the form of an emulsion with a part or all of the oil undergoing the treatment. It is claimed for this method that oils of good colour can be obtained without the removal of unsaturated hydrocarbons, while a further advantage is that the reflux tower is protected from corrosion.

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[30] *Oil and Gas J.*, Sept. 29, 1927.
[31] U.S.P. 1,639,531.

In another process patented by S. J. Dickey and R. C. Wheeler[32] it is claimed that a neutral petroleum distillate can be prepared from an acid treated distillate by first removing the acid sludge by settling and then filtering the oil through dry sand. When the sand becomes clogged the filter is drained from oil and blown with steam and dry air to regenerate it for use again.

The use of sulphur dioxide in the liquid state is well known in the Edeleanu process, which continued to gain adherents in American refining practice; the use of the gas is claimed in a patent granted to P. McMichael[33] in which the oil is agitated with the gas and then filtered through adsorbent material such as fuller's earth or silica gel. Subsequent treatment may include washing with water or weak alkali, treatment with hypochlorite, or with sodium plumbite, or, if necessary, it may be steam distilled. The process is said to be more particularly suitable for cracked distillates.

The hypochlorite process has continued to attract the attention of refiners, and several patents were granted during the year for improvements or modifications of the original method. F. W. Weber[34] forms an emulsion of the oil with water and adds a hypohalite in the form of a fine powder. After agitation the sludge is removed and the oil washed. Then a water soluble reagent capable of generating oxygen, such as hydrogen peroxide or sodium perborate, is added, and the temperature raised and the reaction mixture allowed to settle. After drawing off the aqueous layer the oil is treated with sulphuric acid while being vigorously agitated. After settling and removing the sludge a practically saturated solution of a salt such as sodium silicate is added which reacts with the acid remaining in the oil precipitating a voluminous precipitate which carries down with it the colouring matter in the oil. With very refractory oils the decolorisation and desulphurisation of the oil is brought about by substituting colloidal ferric chloride solution, to which has been added carbonates of rare earths such as are found in Monazite sand, for the sodium silicate reagent.

Improvements in the hypochlorite process are also claimed by H. O. Parker who in one patent[35] proposes to pass the oil into aqueous hypochlorite solution containing excess of caustic alkali, while introducing chlorine into the solution at the point of entry, where it comes in contact with that part of the solution which has the greatest concentration of hypochlorite.

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[32] U.S.P. 1,639,988.
[33] U.S.P. 1,641,546.
[34] U.S.P. 1,636,946.
[35] U.S.P. 1,622,879.

In another patent[36] a continuous treating method is described, the oil passing through a successive series of mixing and settling vessels, the hypochlorite reagent being supplied to one of these, allowed to settle in one of the succeeding vessels and then pumped back to vessels preceding that to which it was first applied.

The application of chlorine is the subject of a patent granted to R. Cross[37], who treats a portion of the oil to be refined with chlorine, and, after exposing this to light, combines it with the main portion.

Still another application of chlorine is that of J. C. Morrell and S. Comay,[38] who advocate the use of copper hypochlorite solution as a refining agent.

The well-known instability of hypochlorite solutions has suggested the desirability of providing the refiner with a reagent less liable to deterioriate as regards its active ingredient. M. P. Appleby and C. Carter have a patent[39] for obtaining a solid dry form of sodium hypochlorite, by mixing a strong solution of the latter with partially or wholly dehydrated salts of an alkaline character, such as sodium metaborate.

The use of selective solvents in refining has been the subject of a few patented processes during the year; one particularly suitable for lubricating oil refining is that of the I. G. Farbenindustrie Aktiengesellschaft,[40] in which the oil is treated with a mixture of methanol and cyclic hydrocarbons of low boiling point, such as benzene, toluene, xylene or cyclohexane, it being claimed that the impurities in crude hydrocarbon mixtures are soluble in such reagents, while the higher boiling point components of the paraffin or naphthene series are not dissolved.

In a process patented by the Burma Oil Company[41] oils are stated to be refined by treating with pure phenol or a mixture of this with cresylic acid containing from 5 to 15 per cent. of water. A method of recovering the phenol for use again is described in the specification.

The use of acetone for deparaffining oils has previously been suggested but has so far gained little favour among practical refiners. In an article by J. Smith[42] it is pointed out that the large volume of the solvent required (80 parts to 1 of oil) makes the use of acetone uncommercial. He suggests the employment of dehydrated isopropyl alcohol, which can be prepared from petroleum

[36] U.S.P. 1,627,338.
[37] U.S.P. 1,623,018.
[38] U.S.P. 1,627,055.
[39] E.P. 274,197.
[40] E.P. 255,905.
[41] E.P. 273,351.
[42] *Oil Age*, Oct., 1927.

cracking plant gases, and cites experiments in which mixtures containing 1 part of oil to 3 of the alcohol gave good separation after centrifuging for 5 minutes at 0° C. and 3000 r.p.m. He further states that the solvent may be used mixed with acetone, and that secondary butyl alcohol also gave good results.

Desulphurisation problems have continued to provide opportunities for intensive research, especially amongst those engaged in refining the sulphurous Mexican and Texan crudes, and those time-honoured reagents, copper and lead, still find advocates and new methods of employment. L. W. Parsons and S. P. Coleman[43] have been granted a patent for a process in which from 1 to 15 per cent. of copper oxide or lead is heated with the oil for half-an-hour at about 150°, the product being then distilled with from 2 to 8 per cent. of caustic soda.

A reagent for treating mineral oils containing sulphur is described by F. C. Axtell[44] and consists of oleum, which has been agitated with excess of benzene, the acid layer separated and used to treat the oil. It is claimed that such acid has no polymerising or oxidising effect.

The Standard Development Company have obtained a patent[45] for a process, according to which the sulphurous oil is treated with sulphur in the presence of a heavy metal sulphide such as that of lead, which has been preformed.

An alkali, which may be in the form of aqueous sodium hydroxide, is also present, and the mixture is agitated with air, the sulphur present being equal in amount to one-half that which is present in the oil as mercaptan. Under the conditions cited the mercaptans are stated to be converted into polysulphides.

Treatment with sulphuric acid or distillation at a temperature not higher than 320° F. completes the process.

A somewhat novel reagent is covered by the patent of T. Hellthaler,[46] who claims the use of Titanium tetrahalide diluted by an inactive solid material such as fuller's earth or kieselguhr or by a liquid such as petroleum ether, benzene or chlorinated hydrocarbons. After the treatment the oil is agitated with a basic earth to absorb the acid formed and bleach the oil.

A paper by M. A. Youtz and P. P. Perkins[47] is of interest to refiners as it deals with the action of various desulphurising agents on pure organic sulphur compounds dissolved in naphtha.

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[43] U.S.P. 1,640,720.
[44] U.S.P. 1,645,679.
[45] E.P. 270,626.
[46] U.S.P. 1,643,272.
[47] *Ind. Eng. Chem.*, 1927, **19**, 1247-1250.

A modification of the well-known McAfee process is claimed by a patent taken out by F. W. Hall,[48] according to which vapours of aluminium chloride are brought into contact with a stream of liquid oil at the distillation temperature of the latter.

Recovery Methods.

The conversion of the acid resins obtained when refining petroleum products into neutral bitumens is the subject of a patent process described by F. Wilhelm.[49] According to this, acid tar is heated until it is sufficiently liquid and part of the acid settles out and is removed. The temperature is then raised to 130° C., and either sulphur or hydrogen sulphide added, which causes reduction of the remaining sulphuric acid.

The electrolytic recovery of waste acid is described in a patent by F. M. Rogers, F. M. Grimm and G. L. Wendt,[50] who propose to dilute the acid until its density is 1·38 and electrolyse it at 65°, with a current of from 3 to 3·5 amp. per square decimeter to oxidise the organic matter present.

Sludge alkali is claimed to be converted into a useful material by the process patented by G. Alleman,[51] who heats the sludge with water under a pressure of 4 atmospheres for two hours. The solution is concentrated to separate soaps and resins and then treated in aqueous solution with a metallic salt such as calcium chloride, which gives a precipitate which is said to be valuable as an adhesive or filler.

An interesting article by G. W. Cupit[52] deals extensively with the recovery of by-products from acid sludge, more especially that derived from the treatment of reduced paraffin base crude oils. He describes in detail the procedure to be followed in the manufacture of various kinds of asphalts from the sludge, and shows that products of good quality can be prepared.

Miscellaneous.

Improvements in the quality and stability of lubricating oils is claimed in a patent granted to A. A. Somerville,[53] according at which the addition to the oil of 0·5 to 1 per cent. of diacetoneamine, triacetoneamine or a similar compound formed by condensing ketones with nitrogenous bases is said to produce the improvement referred to, especially with oils used at high temperatures.

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[48] U.S.P. 1,647,445.
[49] E.P. 254,674.
[50] U.S.P. 1,630,074.
[51] U.S.P. 1,637,510.
[52] *The Refiner*, Sept., 1927.
[53] U.S.P. 1,617,826.

An addition to the long list of patents covering the production of bituminous emulsions is provided by the process of H. E. Potts,[54] who uses a liquid factis oil made by the action of sulphur chloride on train oil as an addition to bitumen which has been treated at 210 to 230° F. A solution of caustic soda is added in small portions at a time while stirring and the mixture passed to a Plausen percussion mill, together with about half its weight of water containing a trace of sodium carbonate. The addition of sulphurised resins to the factis oil is stated to give an emulsion which does not soften or become sticky in sunlight.

[54] R.P. 271,177.

Refining in Europe.*

By H. I. Waterman, Ph.D. (Member), and J. N. J. Perquin.

In this review consideration has been given to petroleum products only. The proper refining has been developed continuously without predominant new processes. In high pressure hydrogenation the number of chemists working in this line has greatly increased, and we may mention in this respect Ipatiew and collaborators. Further, it seems that the number of products obtained from carbonaceous raw materials steadily increases, *e.g.*, different species of gasoline, alcohols, prepared from olefines.

There is a tendency to prepare those products which are most advantageous. In this respect the chemistry gradually governs the refining methods. We especially draw attention to the manipulations with the waste gases for hydrogenation and other purposes. In the following survey the subject is divided into chapters :—(1) Treatment, (2) Products obtained ; (3) Analysis ; (4) Research.

1. Treatment.

(*a*) *Refining.*—A. Rauch[1] describes the use of fuller's earth. B. Neumann[2] gives a review on the action of different bleaching earths. This review contains the measuring of the activity, the changes occurring by heating and a theoretical discussion on the mechanism of the bleaching action. F. Weldes[3] investigated the reaction of acids on bleaching earths, which increased the

* Paper received August 2, 1928.
[1] *Journ. Inst. Petr. Techn.*, 1927, **13**, 325.
[2] *Z. f. angew. Chem.*, 1927, **40**, 337.
[3] *Ibid.*, 79.

activity. This increase in activity is caused by dissolving the aluminium and iron compounds, thus changing the physical properties of the earth. Treating with NaOH decreases the activity. R. A. Wischin[4] calls attention to the use of floridin for the refining of cracked gasoline; also for the refining of lubricating oils, used or other waste oils. Dr. Typke[5] discusses the different methods of regenerating lubricating- and transformer-oils, which are practically in use. M. Cornet[6] concludes that there is no connection between the percentage of sludge formed in treating an oil with sulphuric acid and the formation of carbon or tarry materials in using this oil in the internal combustion engines. Typke[7] treats the subject of the refining of transformer oils and especially discusses the Edeleanu process.

(*b*) *Polymerisation.*—M. Otto[8] investigated the polymerisation of gaseous olefines with boron fluorid (BF_3). As at normal pressures only a few bubbles of BF_3 are sufficient to change the liquid isobutylene into a viscous oil by polymerisation, working with ethylene and propylene, higher pressures are required. The experiments were carried out in two autoclaves of 280 and 530 c.c. The best results were obtained at room temperature. In the small bomb with 100 gr. C_2H_4 and 10 gr. BF_3 (130 atm. initial pressure) all the ethylene was polymerised in 10–12 hours (final pressure 20 atm.). In the larger autoclave Otto obtained from 100 gr. ethylene and 10 gr. BF_3 (70 atm. initial pressure) only 25 gr. of an oil in 14 hours. By filling the bomb with asbestos, 60-70 gr. oil were formed at the same time. The velocity of the process is extremely increased by the presence of nickel. The influence of other catalysts is also investigated. The BF_3 is easily removed from the polymerisation products by heating. The oils obtained are of good quality and are comparable with American lubricating oils. The viscosity of the product depends on the circumstances of the experiment.

2. Products Obtained.

(*a*) *Gasoline.*—H. Y. V. Jackson[9] discusses the relation between the specifications of petrol and the actual behaviour in internal combustion engines, and gives in a general way the design and operation of engines required to run on such spirits.

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[4] *Chem. Zeit.*, 1927, **51**, 181.
[5] *Erdöl u. Teer*, 1927, **3**, 282-299.
[6] *Chim. et Ind.*, 1927, **19**, No. 4, 281.
[7] *Chem. Zeit.*, 1927, **51**, 628.
[8] *Brennstoff-chem.*, 1927, **8**, 321.
[9] *Journ. Inst. Petr. Techn.*, 1927, **13**, 855.

(*b*) *Kerosine.*—W. Woodrow[10] discussed the uses of kerosine such as for illumination, extraction of naphthalene from coal gas, insecticides, oil engine fuel, incubator work and for cookers. S. Bowman[11] describes the different causes of formation of char, the tendency to smoke and the rate of consumption.

(*c*) *Transformer and Lubricating Oil.*—J. W. Donaldson, "The Volatility and Carbonisation of Oils for Cylinder Lubrication"[12]. The points which have to be considered in selecting an oil for cylinder lubrication in a heavy-oil engine are whether to use a large quantity of a light oil which will volatilise rapidly at a lower temperature and leave a smaller deposit, or to use a smaller quantity of a heavy oil which will volatilise slower at a higher temperature but which will leave a much heavier deposit. Generally it is advisable to use the minimum quantity of as light a bodied oil as possible, consistent with good lubrication and the temperature of running parts, so as to obtain the smallest quantity of carbon deposits.

(*d*) *Other Products.*—P. Kogerman[13] investigated Estonian shale-oil. In Part I he describes the isolation and properties of phenols. The phenol content of the shale-oil was determined, such as the effect of the concentration of sodium hydroxide solutions used on the result of the analysis. A slight reduction of phenols due to redistillation has been shown in two series of experiments and an improved method for the determination of phenols in tars (or oils) is described, which gives fairly consistent results. For the first time a shale-oil very rich in phenols has been examined carefully and different constituents isolated and identified. O. m. and p. cresols were determined almost quantitatively, whilst the presence of 1-4-5-1-2-4- and 1-3-4-xylenols were established and the presence of higher phenols such as mesitol and propylphenol was suspected. The phenols of kukersite oil closely correspond to those of low-temperature coal tars, but the former contain phenolic ethers, which so far have not been reported in researches in coal tar. Pyrocatechol has been identified in the water fraction obtained by distillation of the oil. When treated with strong sodium hydroxide solution, the fraction of b.p. 230°–270° is completely resinified. This might be regarded as a new and very simple method for the preparation of phenolic resins.

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[10] *Journ. Inst. Petr. Techn.*, 1927, **13**, 398.
[11] *Ibid.*, 410.
[12] *J. Soc. Chem. Ind.*, 1927, **46**, 324 T.
[13] *Ibid.*, 142 T.

A. Laurent[14] propagates his "targol," a product obtained by mixing the gasoline hydrocarbons with terpenes oxidised beforehand by heating with air.

Nielsen and Baker[15] prepared lubricating oil from coal by the so-called "L and N" process, which is a low-temperature carbonisation process in which superheating is carefully prevented. They tested their lubricating oil in an oil-testing machine, and it seemed to be of a good quality.

3. Analysis.

(*a*) *Crude Oil.*—A. Ashworth[16] constructed a pipe still for continuous distillation in the laboratory; this apparatus has great advantages and may be used for observing the equilibrium temperature of light distillates as well as for distillation of water-containing oils.

J. Marcusson[17] gives a new method for the determination of the asphalt content of mineral oils. His method consists in quantitatively flocculating by treating with a solution of ferric chloride in ethyl ether. The asphaltenes are transformed into insoluble double compounds. After washing the precipitate is decomposed with hydrochloric acid. The asphalt thus obtained is weighed.

(*b*) *Gasoline.*—Weerman[18] gives an easy method for determining the self-ignition temperature of a petrol. In the apparatus used he tested the influence of a great many compounds of 22 elements, which are given in a table. The compounds, which have a good anti-knock effect, produce a very considerable increase in self-ignition temperature.

C. I. Kelly[19] studied the factors affecting internal combustion.

G. Maxwell[20] discusses the different theories as to the cause of pinking and the different factors affecting pinking.

The anti-knock problem is further discussed by different authors, *e.g.*, by A. Egerton and S. Gates[21].

R. Moutte[22] continues the work of Dixmier on the analysis of mixtures of hydrocarbons by the refractometric dispersivity $\frac{\Delta n}{d}$. He considers the wavelengths $\lambda_1=589\ \mu\mu$ and $\lambda_2=436\ \mu\mu$. In

[14] *Chim. et Ind.*, **19**, No. 4, 319.
[15] *Brennstoff-chem.*, 1927, **8**, 289.
[16] *Journ. Inst. Petr. Techn.*, 1927, **13**, 91.
[17] *Chem. Zeit.*, 1927, **51**, 190.
[18] *Journ. Inst. Petr. Techn.*, 1927, **13**, 300.
[19] *Ibid.*, 101.
[20] *Ibid.*, 224.
[21] *Ibid.*, 244, 256, 273 and 281.
[22] *Chim. et Ind.*, **19**, No. 4, 262.

many cases the determination of the dispersivity will give us useful results in gasoline analysis.

A. Javelle[23] investigates the magnetic rotation of polarisation and for a series of hydrocarbons belonging to different groups, gives a survey of the constant of Verdet connected with the wavelength $546\mu\mu$ (k_1); hexane (18·3° C.) $1{\cdot}46.10^{-2}$, heptane (21·4°) $1{\cdot}51.10^{-2}$, octane (20·6°) $1{\cdot}52.10^{-2}$), benzene (20·8°) $3{\cdot}38.10^{-2}$, toluene (20·3°) $3{\cdot}08.10^{-2}$, ethyl-benzene (20·8°) $3{\cdot}03.10^{-2}$ cyolchexane (20·1°) $1{\cdot}47.10^{-2}$, dimethylcyclohexane (18·3°) $1{\cdot}58.10^{-2}$, cyclohexene (20·6°) $1{\cdot}747.10^{-2}$, methylcyclohexene ortho (18·25°) $1{\cdot}71.10^{-2}$, methylcyclohexene para (18·5°) $1{\cdot}75.10^{-2}$, methylcyclohexene meta (18·4°) $1{\cdot}753.10^{-2}$. He worked with two component mixtures cyclohexane-toluene, cyclohexane-benzene and cyclohexene-toluene and found that the changes in the values followed the law of additivity of Biot.

J. Brame and T. Hunter[24] describe a research about the methods of separating the different constituents of a cracked spirit. In Part I. of the paper they tried to find a method of separating unsaturated and aromatic hydrocarbons, saturated paraffins and naphthenes. Whilst this problem has not been solved, they applied a novel method to the difficult problem of separating by fractional distillation two hydrocarbons of not dissimilar boiling points by adding a third component, *e.g.*, aniline or methyl-alcohol, to the binary mixture. In Part II. of the paper they applied the results of the research described in Part I. on the determination of the components of a cracked Russian kerosine from a Cross-plant. They proved the presence of paraffins and isoparaffins, *e.g.*, hexane, isohexane, etc., naphthenes in nearly equal quantities as the paraffins. Olefines of the type $R\,CH{=}CH^2$ appeared to be absent, 3-2 methyl pentene and 4-5-methylhexene were probably present, diolefines-cyclic olefines predominant among the unsaturates boiling between 90° and 120°, aromatics only in small percentages were present.

(*c*) *Kerosine.*—J. Kewley and J. S. Jackson[25] studied the burning of mineral oils in wick-fed lamps, especially the influence of different factors on the candle-power, on the tendency to smoke, on the carbonisation of the wick, etc.

W. Thomas[26] gives details on the burning-test of kerosine with various types of lamps.

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[23] *Chim. et Ind.*, **19**, No. 4, 264.
[24] *Journ. Inst. Petr. Techn.*, 1927, **13**, 794.
[25] *Ibid.*, 364.
[26] *Ibid.*, 402.

(*d*) *Transformer and Lubricating Oil.*—H. Vogel[27] discusses the phenomena of melting and solidifying of oils, which is of importance for testing transformer and lubricating oils, and gives a new method for the determination of the pour point, which is accurate at 1° C.

N. Butkow[28] compares the different methods of testing transformer-oils on oxidation, and gives a new method which differs from the ordinary sludging value. The sludging is tested by heating 10 c.c. of the oil in a calorimetric bomb during only two hours at 150° C. under a pressure of about 15 atm. of oxygen. From the thus treated oil he determined the acid-value, saponification-number and the percentage absorbed by strong sulphuric acid.

He shows that unrefined oils will less oxidise than the same oil after refining with oleum.

He further[29] described the oxidation of turbine oils, and showed also with this oil a better result on resistance to oxidation when the oil was normally refined than after refining with 10-15 per cent. oleum. He also proved this practically.

He tries to explain this by assuming that on further refining the anti-oxydants are removed. For the testing of this oil he used his method with oxygen under pressure during four hours. The normal sludging-value gives no good results because this oil is not easily oxidisable.

H. Young[30] propagates a direct oil corrosion test. The test is performed by means of an apparatus whereby warm oil (at about 90° C.) is run continuously over warm steel, white metal, brass, copper or any other metal. He stated that corrosion occurs by H_2SO_4 content of the oils; a sulphate value of more than 0·55 per cent. is an indication that the oil is dangerous to use. By the D.O.C. test as little as 0·002 per cent. H_2SO_4 can be determined.

G. Dixmier[31] investigates on standard methods for the determination of the quantity of asphalt, or carbon formed on heating mineral oils in connection with their behaviour in the engine.

A. R. Matthis[32] gives a test for the investigation of transformer oil. The oil is heated at 170° during 5 hours. The ratio of surface exposed to the volume of air among others is of high importance. He also determines the acidity of the oil heated till the beginning of formation of deposits. Thus he investigates the behaviour

[27] *Erdöl u. Teer*, 1927, **3**, 534.
[28] *Ibid.*, 551.
[29] *Ibid.*, 823.
[30] *Journ. Inst. Petr. Techn.*, 1927, **13**, 760.
[31] *Chim. et Ind.*, **19**, No. 4, 282.
[32] *Ibid.*, 324.

of the oil towards oxidation. The same author[33] gives valuable information about practical tests for the determination of humidity in transformer oils.

4. Research.

(*a*) *General.*—N. Butkow[34] investigated the influence of β-naphthol on the oxidation of transformer oil by air. One per cent. of β-naphthol considerably decreases the oxidation of the oil. The experiments were taken with Emba (Russian) transformer oil. The oxidation was carried out at 150° and 10-15 atm. The treated oil had an acid value of 16·76, a saponification number of 38·26 and a loss to H_2SO_4 of 23 per cent. The treated oil mixed with 1 per cent. β-naphthol gave respectively 0·35, 2·06 and 3 per cent. He also determined the constitution of the resulting gases after treatment during 3 hrs. at 150° C., which consisted of 8·8 per cent. CO_2, 59·2½ per cent. O_2 and 10 per cent. CO with 1 per cent. β-naphthol. Practically no oxidation took place. β-Naphthyl amine and some other compounds have the same influence.

(*b*) *Gasoline.*—Lewis[35] investigated the oxidation of hydrocarbons. To that purpose he heated the hydrocarbons at constant volume. On slowly heating in the presence of air the temperature-pressure curves showed a typical inflection at a certain temperature, which he called the critical inflection temperature, caused by increasing molecule number. This temperature is different, for each hydrocarbon depends on the heating, the concentration on the vapour and on the presence of water. The influence of the walls was investigated just as that of some catalysers. One per cent. tetra-ethyl lead prevented the decomposition. The unsaturated hydrocarbons decompose easier and the paraffins exploded sooner. This is caused, in the author's view, by the large amount of heat which is set free at the reaction

$$C_nH_{2n+2}+O \longrightarrow C_nH_{2n}+H_2O+\times\text{cal.}$$

This heat will be more than the heat of compression in the combustion engine.

D. Freund[36] discusses the oxidation of gasoline by air at 400-500° C., and states the formation of acids, ethers, alcohols and phenols, while unsaturated and aromatic hydrocarbons are formed in the same time by cracking.

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[33] *Chim. et Ind.*, **19**, No. 4, 328.
[34] *Erdöl u. Teer*, 1927, **3**, 267.
[35] *J. Chem. Soc.*, 1927, 1555.
[36] *Z. f. angew. Chem.*, 1927, **40**, 368.

(c). *Berginisation.*—W. Ormandy, E. Craven, T. Heilbronn and H. Channon[37] studied the berginisation of fish-liver oils and pinene as a contribution to the problem of the origin of petroleum.

A. Spilker[38] gives a survey on the liquefaction of coal.

H. I. Waterman and J. N. J. Perquin[39] continue their research work on berginisation. They compared the products which are formed by cracking of paraffin wax at 450° with those obtained in berginisation. They especially investigated the gasoline fractions. The boiling point curves of both gasoline types were interrupted and distinctly showed very pronounced maxima at the boiling points of the normal hydrocarbons, *i.e.*, pentane, hexane, heptane and octane. In berginisation the percentage of these hydrocarbons was higher than in cracking. The products of berginisation are more stable than those obtained in cracking. Even after one year the refractivity had only changed slightly.

The berginisation product contains olefines, the percentage is 10 per cent. in the hexane-, heptane- and octane-fractions. The cracking distillates are more unsaturated, the bromine number, the specific gravity, the refractive index and the dispersivity are higher, the aniline point is lower The products of cracking are much more unstable and soon increase in specific gravity and refractivity.

It seems that between the maxima of the normal aliphatic hydrocarbons there are other types with higher dispersivity and lower bromine number and aniline point.

A. Kling et D. Florentin[40] continue their work on hydrogenation. Naphthalene and anthracene at high temperature are hydrogenated by molecular hydrogen of high pressure. The formation of hydronaphthalenes and of hydroanthracenes is accompanied by the appearance of small quantities of benzene hydrocarbons which find their origin in the rupture of one of the benzene nuclea. The limit of temperature below which no hydrogenation occurs depends on different circumstances, *e.g.*, the initial hydrogen pressure.

Naphthalene and anthracene have the limits 475° and 440° The use of appropriated catalysers, *e.g.*, $FeCl_3$ lower these temperature limits.

W. A. Dyes[41] gives a survey on the liquefaction of lignite and coal, in which paper special attention is given to the commercial side of this problem.

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[37] *Journ. Inst. Petr. Techn.*, 1927, **13**, 1.
[38] *Braunkohle*, 1927, **26**, 545; *Chem. Abstr.*, 1927, **21**, 40-47.
[39] *Rec. Trav. Chim. Pays-Bas*, 1927, **46**, 813.
[40] *Bull. de la Société chim. de France*, 1927, 4th series, **41-42**, 864.
[41] *Chem. Zeit.*, 1927, **51**, 853-873.

Dr. Krauch, Director of the "I. G. Farbenindustrie" A. G. held a lecture which is published in *Petroleum Zeitschr.*, October 10, 1927 (1), on the Haber-Bosch synthesis of NH_3, while a new type of generator for the production of H_2 from brown coal is described, and (2) on coal-liquefaction. The process of dry distillation of coal and brown-coal is treated also, the research of the Badische Anilin and Sodafabrik in which liquid products were obtained from coal by passing CO and H_2 over catalysts. The last mentioned process leads to the synthesis of methanol, to the production of higher alcohols and of hydrocarbons. Direct hydrogenation of coal is further treated. After mentioning the work of Bergius, the process of the I. G. Farbenindustrie is described, which is worked out on a large scale in Leuna. In the process different types of catalysts are applicated by which the reaction is carried out into a definite direction. The I. G. Farbenindustrie also tried to apply other influences on the reaction velocity such as exact and definite radiation energy electric fields and discharges.

N. O. Orlow[42] studied the transformations of phenanthrene at heating in the presence of hydrogen with aluminium oxide in the iron-apparatus used by Ipatiew. Dihydrophenanthrene, alkylnaphthalene, naphthalene and its dissociation products were formed.

W. Ipatiew and N. Orlow[43] investigate the processes of decomposition of some aromatic compounds under hydrogen pressure and under the influence of catalysts, *e.g.*, pure aluminium oxide alone or mixed with Cu- and Fe-oxide. The temperature was kept at at least 400° C. Below this temperature the reaction velocities are too small.

In the absence of hydrogen phenol alters but slowly in the heating with aluminium oxide at 450°. After four hours' heating in the presence of hydrogen under the same conditions phenol gives 20 per cent. of the theoretical yield of benzene. Under the same conditions o-cresol yields 30 per cent. of a mixture of benzene and toluene.

These and analogous observations are of importance for the process in which tar products are treated with high pressure hydrogen.

A. W. Nash gives a survey on the possible auxiliary sources of liquid fuels[44].

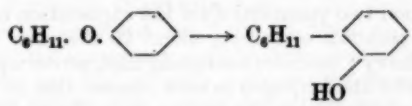
(*d*). *Cracking.*—J. Varga and Erdély[45] describe a laboratory method for cracking different oils. They obtained from gas oil about 57 per cent. from refined brown coal tar oils about 47 per

[42] *Ber.*, 1927, **60**, 1950.
[43] *Ibid.*, 1963.
[44] *Journ. Inst. Petr. Techn.*, 1927, **13**, 681.
[45] *Brennstoff-chem.*, 1927, **12**, 133.

cent. from crude tar oils 31 per cent. to 200° C. boiling gasolines. The products obtained from refined tar oil behave like cracked petroleum products; crude tar oils with 48-58 per cent. phenols formed gasolines which were for 35-47 per cent. soluble in NaOH solution. The decomposition of tar oils at 10 atm. begins at 370°–390° C., this temperature is about 20° higher for petroleum gas oils.

In a summarizing paper Waterman and Perquin[46] give an experimental survey of the refractive indices and dispersive power of several samples of hydrocarbons of different groups. Different examples are given to prove the use of refraction values in investigations on the purity of hydrocarbons. This method of investigation was applied to the products obtained by cracking paraffin wax in the vapour phase, this process being carried out in vacuum. Notwithstanding the high temperature used (450°–460° C. for four hours) no cracking occurred, the reason being that the time in the cracking spiral was only four seconds.

S. Skraup and W. Beifusz[47] continue their work on the decomposition of organic compounds on heating. They now examine some cyclohexane-derivatives. Cyclohexyl phenylether was transformed into o-cyclohexyl phenol:



They express doubt to the considerations of Aschan about the transformation of cyclohexane into methylcyclopentane on heating during eight hours at 330°. At 350° heating during three days S. and B. found that the cyclohexane had not changed.

A. E. Dunstan, R. Pithethly and E. S. L. Beale[48] prepare aromatic hydrocarbons by cracking the residue obtained in the process of purifying mineral oils with SO_2.

L. Singer[49] discusses the different processes to obtain in one operation gasoline with defined boiling point curve from heavy oils. The cracking process is combined with a fractional distillation.

(*e*). *Synthesis.*—O. C. Elvins[50] studied the synthesis of hydrocarbons from water-gas. The results are found in the following conclusions:

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[46] *Journ. Inst. Petr. Techn.*, 1927, **13**, 413.
[47] *Ber.*, 1927, **60**, 1070.
[48] E. P. 250,701, 1925.
[49] *Chem. Zeit.*, 1927, **51**, 170.
[50] *J. Soc. Chem. Ind.*, 1927, **46**, 473T.

1. Olefins may be obtained by conversion of water-gas. From these may be obtained compounds containing oxygen.
2. It is preferable, to use fairly large granules of catalyst to obviate clogging of the contact tube, due to the formation of solid hydrocarbons.
3. Catalysts prepared by precipitation shrink on reduction, with consequent loss of activity.
4. Fused oxide catalysts may be used, which fact effects a great saving in time of preparation over other methods and also give a hard stable granule.
5. The oxygen of carbon monoxide may be eliminated almost entirely as carbon dioxide when hydrocarbons are formed.

Fischer and Tropsch[51] describe the preparation of high molecular paraffins of about 70 carbon atoms mol. w. at about 1000 by heating water-gas at 10–15 atm. at 250° C. in the presence of an iron-copper catalyst, at the same time oxygen containing products and lower hydrocarbons being formed. The higher paraffins remain in the contact mass, from which they were extracted with benzene.

Franz Fischer and H. Tropsch[52] give some details on the synthesis of solid paraffins from CO.

They mention two possibilities for the explanation of the formation of such paraffins containing about 70 C-atoms. The first is the carbide-theory; carbides containing high percentages of carbon would react with the hydrogen in such manner that in the presence of CO this hydrogen takes the carbon from the carbide and thus gives the hydrocarbons. The second theory is the possibility of the primary formation of CH_2 from the carbides which then polymerises to higher hydrocarbons, in which process eventually free valences may be saturated by hydrogen. This also explains the formation of completely hydrogenated cyclic hydrocarbons.

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[51] *Brennstoff-chem.*, 1927, **8**, 165.
[52] *Ber.*, 1927, **60**, 1330.

American Refinery Technology.*

By Benjamin T. Brooks, Ph.D., F.C.S. (Member).

The second report of the Federal Oil Conservation Board, made public by Secretary Work last January (1928), dealing with possible petroleum and motor fuel substitutes and shale-oil is probably of great value in educating the public, although the facts presented are very generally known in the oil industry and to technologists in general. The report may be summarized as follows :—

(1) There is no substitute for petroleum gasoline available or capable of being manufactured in sufficient quantities except at very much higher cost than the present refinery cost of gasoline.

(2) *Shale-oil.*—The estimated costs of mining the shale vary from \$0·40 to \$2·50 per ton. The yield of crude shale-oil is probably 30 to 50 gallons per ton. The Board does not attempt to estimate what the manufacturing cost of shale-oil, or motor fuel from that source would be.

(3) *Coal.*—(*a*) The Bergius process. The general facts known to the public are reviewed. The process produces 93 to 133 gallons of crude oil of which about 40 gallons is motor fuel, per ton of coal. The pressures employed are 2,100 to 2,800 lbs. at 800–900° F. The cost of the equipment and the daily production has not been made public, but one naturally compares the general conditions of the Bergius process with present day oil cracking, in which a unit costing about \$225,000 handles about 2,500 to 3,000 barrels of charging stock per day, producing 1,000 to 1,200 barrels of gasoline, at operating pressures of 200–250 lbs. Nevertheless, it is of interest to note that recent developments in oil cracking have been away from large reaction chambers, and experimental oil cracking is quietly being carried out at pressures up to 3,000 lbs.

(*b*) The Board also discusses the possibility of producing gasoline by the hydrogenation of water gas.

(*c*) With regard to benzol and alcohol, too much publicity can hardly be given to the facts. With regard to the distillation of coal, either at high or low temperatures, the Board states, " It is obvious that distillation processes could not be operated for oil production alone, but must depend upon the market for the major products, that is coke and gas, the market for which is limited."

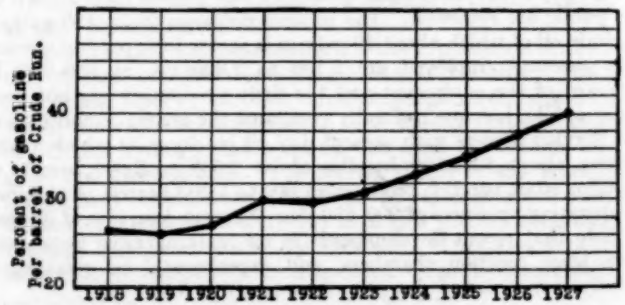
(4) *Alcohol.*—The world's production of molasses, if fermented to alcohol, would be equivalent to less than 2 per cent. of the gasoline

* Paper received June 22nd, 1928.

consumed in the United States in 1926. "If corn were to furnish the only substitute for gasoline we now use, two-thirds of the total tilled acreage of the farms of the United States would be required for this purpose alone."

No attempts have, up to the present, been made in the United States to operate either the Bergius or water gas processes for the production of gasoline on a commercial scale. A laboratory study of hydrocarbon synthesis from water gas has been made by Smith, Davis and Reynolds[1], who state that with a catalyst consisting of metallic cobalt, manganese oxide and a small proportion of copper, under the most favourable conditions, 1,400 cubic feet of water gas were required per gallon of liquid oil. At a cost of 20 cents per M. for water gas this is a material cost of 28 cents per gallon, or about four and a half times the average refinery cost of gasoline during the past year.

The continued increase in the proportion of gasoline produced in American refineries is shown by the statistics, which have been plotted by Ziegenhain[2], as shown in Fig. 1.



Graph showing percentage of gasoline recovered per barrel of crude oil refined. Includes gasoline from crude oil direct, gasoline made by cracking heavy fractions and natural gasoline blended at refineries.

Fig. 1.

Better engineering has done a great deal to reduce labour costs. Mills has recently described the operations of the Richfield refinery near Los Angeles, which runs about 45,000 barrels of crude per day with a total force, including the office, of less than 100 men,

[1] *Ind. and Eng. Chem.*, 1928, **20**, 462.
[2] *Oil and Gas Journal*, December 1st, 1927, p. 178.

most of these men working in eight hour shifts. The 1,800 horse power boiler plant is operated by one man, the gas recovery absorption plant by one foreman and three operators, and a battery of four Cross cracking units are operated by one superintendent and thirteen operators. In many cases, in the past, refineries maintained large fabricating shops in which most of their equipment was built. The much more efficient modern equipment of the best refineries to-day is not so easily thrown together, and since the competition between engineering and equipment concerns, employing competent specialists, is very keen, the elaborate and expensive fabricating shop in the refinery with its high labour and maintenance costs is now unnecessary, and in most cases highly inadvisable, except for simple equipment. The superiority of the pipe still and bubble tower combination has compelled refiners having old-fashioned shell still batteries to improve them. Stratford[3] has described the results of equipping shell stills with rapid oil circulation and forced draft heating. One set of four 10 ft. by 40 ft. stills was so equipped, 750 gallons of oil per minute being delivered through jets close to the still bottom. A charging capacity of 5,300 barrels per still per day was attained, vaporizing 42 per cent. This was a through put of more than five times the former capacity of the still without agitating steam. Another set of six stills 12 ft. by 45 ft. were equipped with oil circulating pumps, discharging 1,100 gallons per minute against the bottom. No radiant or convection coils were applied. The stills were operated as individual units and were run at a capacity of 6,500 barrels per day each, 40 to 50 per cent. being vaporized. These stills are operated in conjunction with bubble towers.

Bell [4] has discussed the advantages and flexibility of pipe still and bubble tower combinations. Numerous diagrammatic flow charts are given and the Marland pipe still, illustrated in this review last year, is described. A radiant heat pipe still installed by the Simms Oil Company is provided with eight carborundum tunnels; the pipe coil is 4-inch tubing having an effective surface of 6,600 square feet. The unit has a daily capacity of 2,500 barrels, taking over 17 per cent. gasoline and 47 per cent. pressure still charging stock.

Another adaptation of bubble towers to shell stills may be seen in the Kanotex refinery. Running continuously the daily capacity of the battery has been raised from 3,000 to 10,000 barrels. Re-running of the gasoline and kerosine is not necessary.

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[3] *Nat. Petr. News*, February 29th, 1928, p. 63; March 7th, 1928, p. 60.
[4] *Nat. Petr. News*, February 29th, 1928, p. 97.

De Florez [5] has pointed out that in the continuous operation of pipe still bubble tower units it has generally been found more desirable to alter the rate of firing, maintaining the flow constant. Automatic temperature regulation has repeatedly been emphasized by De Florez.

The use of radiant heat in tube stills has been discussed by Primrose.[6] The data taken during operation of a tube still having a radiant heat section, operating on Pennsylvania crude and vaporizing 90 per cent., is shown in Table 1.

TABLE 1.

	Coal.	Fuel Oil.
Fuel burned		
B.Th.U. value of fuel	12,800/lb.	136,000/gal.
Throughput—42 gallon barrel per day	1,900	1,830
Temperature of oil entering tube still, ° F.	290	270
Temperature of oil leaving tube still, ° F.	760	770
Vaporization, per cent. of throughput, as shown by bottoms plus excess vaporization	90·0	90·0
Temperature of gases entering convection surface, ° F.	1,120	1,010
Temperature of gases leaving convection surface, ° F.	355	385
Temperature of steam leaving superheater, ° F.	660	670
Pressure of steam entering superheater (moisture 2%)	26	24
Weight of steam used per hour	1,390	1,600
CO_2 in furnace, per cent	15·0	13·0
CO_2 in flue, per cent.	14·3	11·5
Fuel consumption, pounds or gallons per hour	980	100 gal.
Estimated B.Th.U. per hour absorbed in convection surface	3,740,000	3,580,000
Absorbed in convection bank (total)	4,030,000	3,945,000
Absorbed in radiant surface	6,600,000	6,780,000
Absorbed in unit (total)	10,630,000	10,725,000
Estimated thermal efficiency, per cent.	84·8	79·0
Transfer, B.Th.U. per hour per sq. ft. inside surface to oil in convection section	4,250	4,070
Transfer, B.Th.U. per hour per sq. ft. inside surface to oil in radiant section	6,680	6,870
Total inside surface in convection section		880 sq. ft.
Total inside surface in radiant section		987 sq. ft.

According to Nash [7] the following advantages may be secured by the use of radiant heat :—

(1) Higher rates of heat input into the oil without danger either to the structure or the product.

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[5] *Nat. Petr. News*, February 22nd, 1928, p. 49.
[6] *The Refiner*, March, 1928, p. 87.
[7] *Nat. Petr. News*, February 22nd, 1928, p. 70.

(2) More uniform heat input over the entire absorbing surface since the variable of excessively high temperature gases is eliminated.

(3) Correspondingly smaller and less expensive units for the same throughput.

(4) Better fuel economies, since there is no necessity for large quantities of excess air.

(5) More uniform heating keeps the formation of coke and fixed gases at a minimum.

(6) Reduces the time lost by shut down and cleaning of cracking coils.

The results of recirculating a portion of the flue gases in a convection type of furnace in connection with oil cracking are given in Mekler,[8] see Table 2.

TABLE 2.

Oil Consumption and Fuel Efficiency of Still under Different Operating Conditions.

8,000,000 B.Th.U. Convection Input in the Oil; 500,000 B.Th.U. Loss in Furnace.

	Fuel required, pounds.	Heat supplied by fuel, million B.Th.U.	Excess air. %	CO_2.	Loss of heat in flue gases, million B.Th.U.	Oil heating efficiency.
No recirculation .. No recuperation ..	1320	24·8	230	4·8	16·3	32·2
Recuperation only .. Air preheat 800°F., net	727	13·7	500	2·8	5·2	58·3
Recirculation only .. 4.62 : 1 no air preheat	602	11·3	25	12·4	2·8	70·6
Recirculation 1 : 1 .. Air preheat 650°F., net	717	13·5	204	5·1	5·0	59·2
Recirculation 2·5 : 1.. Air preheat 300°F., net	649	12·2	91	8·3	3·7	65·5
Recirculation 3 : 1 .. Air preheat 500°F., net	580	10·9	85	8·5	2·4	73·4

Peterkin,[9] in discussing an ideal distillation unit, states, "So far as the mere ability to put heat into an oil is concerned, it would appear that the pipe still has taken us far along the road to an ideal." Formerly, in the initial distillation of the crude (a 36° Mid-Continent is used for the comparison) a heat input of 32 per cent. was common practice and anything better than 50 per cent. was a rare thing. Table 3 gives a comparison of former shell still practice with boiler and pipe still heating.

[8] *Bull. Am. Inst. Mining and Met. Eng.*, Preprint (1928).
[9] *Oil and Gas J.*, January 5th, 1928, p. 64.

TABLE 3.

Comparison of Heat Balance.

Pipe Still *v.* Boilers.

	Shell still, hand fired, No. 2 Buck.	No. 3 Buckwheat, stoker fired.		Fuel oil.		Bituminous coal.	
		Boiler.	Pipe still.	Boiler.	Pipe still.	Boiler, stoker fired.	Pipe still, pulverized coal.
Total surface in radiant heat zone in per cent. total surface	50·0	20·0	5·5	20·0	16·0	20·0	16·0
B.Th.U. absorbed per hour—							
Per sq. ft. radiant surface ..		13,000	11,500	13,000	9,800	13,000	9,800
Per sq. ft. convection surface .		3,500	1,530	3,500	1,680	3,500	1,680
Per sq. ft. total surface		5,400	2,080	5,400	2,980	5,400	2,980
Heat balance—							
Per cent. heat absorbed ..	32·0	72·5	56·5	81·0	76·2	75·0	75·0
Loss of moisture and hydrogen in fuel	4·0	4·0	4·5	7·0	7·1	5·7	4·7
Dry stack loss ..	36·0	10·9	21·0	9·0	13·2	9·8	16·7
Ashpit loss ..	12·0	9·1	14·0	0·0	0·0	6·5	0·1
Radiation, etc. ..	16·0	3·5	4·0	3·0	3·5	3·0	3·5

An analysis of the use of process steam in refineries is given by Peterkin.[10] As pointed out by him, the aggregate expenditure for steam was and still is the largest single item of the cost of refining petroleum, and, considering all finished products, is of the order of one-quarter of the total operating expense. For every gallon of crude oil processed to finished products, more than a gallon of water has been converted into steam. The main items in rationalizing the use of steam in refineries are :—

(1) The total amount of steam necessary for heating which can be converted to hot water, and the percentage of such heating which can be accomplished by steam delivered at a pressure substantially below the boiler pressure carried, i.e., exhaust from pumps, etc.

[10] *Chem. and Met. Eng.*, 1927, **34**, 544.

(2) The amount of steam necessary in processes where its use is imperative and therefore non-competitive, and the percentage of this consumption which can be supplied by exhaust.

(3) The cost of electrical power generated by steam, as compared with central station, Diesel or gas engine generation, and, if cheaper, the quantity of such power required.

The largest "imperative" use of steam for processing has been n distillation. The wide introduction of the bubble tower type of ractionating towers has reduced the amount of re-running with steam, and the vacuum distillation of lubricating oils is rapidly replacing the fire and steam method. "The question of the use of steam in the processing of petroleum boils down to the simple fact that its use is almost always uneconomical for any purpose other than heating, and then only when condensed and delivered as hot water. Otherwise the industry is rapidly becoming motorized and Dieselized."

O. G. Wilson [11] has calculated charts for determining the sensible heat absorbed or given up by an oil for initial and final temperatures within the temperature range of ordinary refinery operations. These calculations are based upon the formula of Fortsch and Whitman.[12] While the charts may be read to 1,000° F., the data on which they are based extend to about 500° F. Wilson states, however, that experience with these charts shows that they are satisfactory for engineering purposes to a temperature of 800° F.

Schnetzler [13] has constructed a slide rule for the solution of problems of flow through orifices. In testing refinery equipment for the flow of liquids or gases where no measuring device had already been installed, the use of the sharp edge orifice flow meter, reading the pressure drop through the orifice, gives very satisfactory results. Copies of this slide rule are distributed by the Petroleum Division of the American Chemical Society.

Vapour phase cracking continues to be widely discussed. However, most of the plants installed have been relatively small and are generally regarded as being in the experimental stage. Probably owing to the widespread idea that the field is open with respect to patents, and to the great emphasis which has been put upon anti-knock values of gasolines, and also to the fact that almost any method of heating a tube will give a certain amount of cracked gasoline, a large number of "processes" for vapour phase cracking are being exploited.

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[11] *Ind. Eng. Chem.*, 1927, **19**, 824.
[12] *Ind. Eng. Chem.*, 1926, **18**, 795.
[13] *Ind. Eng. Chem.*, 1927, **19**, 1027.

De Florez, well known for his work in this field, has discussed vapour phase cracking [14] and pointed out that the chief operating problem to be contended with is that of efficient heat transfer. It is not sufficient to have a uniformly heated surface, but some provision must be made for bringing most of the vapour at some time in contact with the heated surfaces, at the same time avoiding overheating, which will cause an excessive production of fixed gas. De Florez believes that the only way to accomplish this satisfactorily is to pass the gases through comparatively small tubes at very high velocity. "It is possible to obtain a yield of approximately 30 per cent. in one pass, together with a production of non-condensibles of between 12 and 15 per cent." "Up to the present no metal of reasonable cost has been available, for the tubes, which would not be oxidized at temperatures of over 1,000° F.; consequently, until some suitable metal becomes available, a fairly rapid deterioration of tubes must be expected and allowed for in the operating expense of a plant." De Florez points out that the charging stock must be an overhead distillate which can be completely vaporized. Pressure distillate bottoms are excellent for this purpose. The fuel consumption is about 10 per cent. of the total charge when no provision is made to recover heat. According to De Florez' experience, the operating costs are approximately 25 cents per barrel charge, which does not include treating and steam re-running of the gasoline. The latter operations cost about 20 cents per barrel of distillate treated.

The vapour phase process operated by the Pure Oil Company at Cabin Creek, W. Va., uses tubes carrying a core of cement and iron oxide. Whether this core functions as a catalyst, or simply in a mechanical way to produce turbulent flow of vapour in the tubes, is not clear. Another process supplies the heat to the vaporized oil by mixing with gas which has been heated by passing through heated checker work stoves, to about 1,400–1,500° F. Another process passes the gases from the tube furnace into a large insulated chamber filled with pumice.

The method of making and testing the large welded reaction chambers used in the Holmes-Manly and Dubbs processes has been described by Jasper.[15] The heaviest welded chambers made in this way weighed 200 tons and are used at 900° F. and 600 lbs. pressure.

The chromium plating of reaction chambers is apparently a successful solution of the corrosion problem as regards this part of the cracking equipment. Chambers so plated have now been in

[14] *Nat. Petr. News*, December 7th, 1927, p. 35.
[15] *Ind. and Eng. Chem.*, 1928, **20**, 466.

use two years, in service where the corrosion of the unplated chambers has been observed to be ½ to ¾ inches per year.

Removal of the very fine suspended carbon from pressure still residuum by treating with ½ per cent. of 37° Bé sulphuric acid, to produce marketable fuel oil, is described by Goodwin.[16]

Corrosion of field tanks by hydrogen sulphide is particularly serious in the Panhandle and West Texas fields. Mead[17] has shown the effect of adding sufficient caustic soda to Crane-Upton crude to neutralize the hydrochloric acid developed on distillation. Under these conditions hydrogen sulphide corrosion is not so serious.

TABLE 4.

Effect of Caustic Soda in Reducing Corrosion.

Lbs. caustic per barrel charge.	Total HCl lbs. per hour.	Total Fe lbs. per hour.	Total H_2S lbs. per hour.
0·0	13·1	11·2	90·7
0·025	0·9	0·3	101·0

Mead and others have observed that iron sulphide, formed by the corrosion of tanks, stills, etc., is capable of oxidation on exposure to the air, and with such rapidity that ignition of oil vapours has been observed.

Generally it does not pay to remove hydrogen sulphide from natural gas by the use of alkalies when the gas is used as an industrial fuel or for making carbon black. There has been a geat deal of discussion of the possibility of treating crudes such as the Panhandle, West Texas, and Luling crudes, which evolve hydrogen sulphide copiously on *distillation*, to avoid this nuisance and attendant corrosion. Most of this hydrogen sulphide is formed during the distillation by the decomposition of sulphur compounds. Panhandle crude also yields free sulphur on distillation, although the crude oil contains no free sulphur. Even if caustic soda were effective in preventing the evolution of this hydrogen sulphide, the tonnages of sulphur which a moderate-sized refinery would have to take care of in this way are so large as to make such a process uneconomic, even if successful. It is purely a question of cost. The cheapest way to get rid of sulphur in oil is to evolve it as hydrogen sulphide and pass it into a stack to the air. Many refiners, as in California, would be delighted to get rid of the sulphur in their oil so easily. Chromium plating has been shown to be effective against hydrogen sulphide at cracking temperatures, and

[16] U.S. Pat. 1,660,295 (1928).
[17] *Oil and Gas J.*, December 8th, 1927, p. 35.

is even more effective at the lower temperatures of crude distillation. But the hydrochloric acid must be taken care of by lime or caustic, as shown by Mead. Condenser tubes and valves can be chromium plated. Cracking tubes, when so plated inside, do not stand the mechanical hammering and abrasion of the cleaning tools used for removing the coke. However, the corrosion due to hydrogen sulphide alone, in crude distillation, is not sufficiently serious to warrant any very expensive method of overcoming it. In this connection the decomposition of various types of organic sulphur compounds investigated by Faragher, Morrell and Corney [18] is of great interest. They passed the sulphur compounds through hot tubes at about 925° F. They observed no decomposition of thiophene, in the short time interval of their experiments, up to 871° C. Ethyl disulphide yielded hydrogen sulphide, sulphur, ethyl mercaptan, alkyl sulphides and thiophene. Propyl disulphide, n. butyl and iso-amyl disulphides gave analogous decomposition products. Diethyl sulphide gave hydrogen sulphide and mercaptans. Iso-amyl mercaptan gave large proportions of hydrogen sulphide, sulphur and no thiophene. They note that Smackover crude containing 2·5 per cent. sulphur gives less corrosion in cracking equipment than Panhandle crude which contains about 0·6 per cent. sulphur. They ascribe the lesser corrosion of Smackover oils to the stablility of the sulphur compounds present, probably thiophenes.

Cracked gasolines made by vapour phase cracking are usually very low in sulphur, most of the sulphur originally present having been evolved as hydrogen sulphide.

An important advance has been made in the refining of gasolines, particularly cracked gasolines, high in sulphur content by refining with sulphuric acid at low temperatures. Halloran [19] reports that the *loss* on treating cracked California gasoline by sulphuric acid under ordinary conditions to meet the 0·10 per cent. sulphur specification, is 30 *per cent.* of the original gasoline. Concentrated sulphuric acid at low temperatures proved to be an excellent solvent for the sulphur compounds and both the polymerization and solution loss was greatly reduced. Much less tar is formed and the acid sludge is much more fluid. The cracked distillate is cooled to —5° F. and treated continuously with acid in several stages. The acid required is 40 per cent. less, the solution loss 30 per cent. less and the polymerization loss 70 per cent. less than when the treating is carried out at ordinary temperatures. Youtz and Perkins [20] have compared the effectiveness of 95 per cent. sulphuric

[18] *Ind. Eng. Chem.*, 1928, **20**, 527.
[19] *Oil and Gas J.*, December 8th, 1927, p. 35; Klemgard, *The Refiner*, May, 1927.
[20] *Ind. Eng. Chem.*, 1927, **19**, 1247.

acid, anhydrous aluminium chloride, and silica gel in the removal of various types of sulphur compounds from straight run gasoline. Sulphuric acid functions as a solvent for the sulphur compounds. Aluminium chloride decomposes disulphides mainly to mercaptans. Hounsell [21] states that sweetening by plumbite solution proved unsatisfactory in the case of cracked gasoline from Smackover crude, and states that ammoniacal copper solution was much more effective. Hounsell [21] also gives the details of chemical control for treating straight run gasolines with hyopchlorite solution. Morrell and Bergmann [22] have prepared very useful charts showing the rate of flow of 66° sulphuric acid and 30° caustic soda solution through orifices under various pressure differentials up to 50 lbs.

The refining losses on treating cracked gasoline by sulphuric acid noted above are, of course, very unusual, and Morrell has published the refining losses resulting on treating a variety of cracked gasolines from Mid-Continent and other oils. The polymerization loss is from about 1·0 to 2·4 per cent., for amounts of acid up to 10 lbs. per barrel. The polymer losses are usually about one half of the total solution and polymer loss.

The Marland Refining Company and others have been using air to reduce the amount of plumbite and sulphur required for sweetening the very sour gasoline from Panhandle and West Texas crudes. Morrell and Faragher [24] state that the function of the air is the oxidation of the precipitated lead sulphide to lead sulphate, which with excess caustic soda then gives more sodium plumbite and sodium sulphate.

Considerable improvement has been made in the recovery and concentration of sulphuric acid from petroleum acid sludge. It was noted in the Russian Patent 10,416 issued in 1907 to Nobel Brothers that digestion of the diluted sludge acid caused the separation of the combined hydrocarbon material. This was also mentioned in a later U.S. Patent to Van Tienen, but the successful commercial operation of the process has apparently only recently been carried out by the digestion of the diluted acid in acid-proof brick-lined digesters. The bricks are set in acid-proof cement, and the process is operated continuously. The concentration of the acid has also been very much simplified by a method developed by the Chemical Construction Company. The new concentration unit is in the form of a brick-lined cylindrical drum divided into two compartments. Hot flue gas is passed first into the concentrated acid compartment

[21] *The Refiner*, March, 1928, p. 59; *The Refiner*, April, 1928, p. 63.
[22] *Chem. and Met. Eng.*, 1928, **35**, 291.
[24] *Ind. Eng. Chem.*, 1928, **19**, 1045.

from which 66° acid is continuously withdrawn. The hot gases from this compartment, containing much SO_3 fume, are then passed into the second compartment containing the dilute acid, where the hot gases are much cooled and deprived of the SO_3 fume. The fume removal in the second compartment is so effective that the use of a Cottrell fume precipitator is generally not necessary. A typical run record is as follows :—

Low unit.			High unit.	
Feed acid ° Bé.	Exit acid ° Bé.	Exit temp. ° F.	Exit acid ° Bé.	Exit temp. ° F.
33	35	195	62	340
33	38	210	66	415
40	43	220	66	415
46	47·2	235	66	415
50·5	51·5	256	66	415

Anti-Knock Gasolines.

Thirty-six refining companies are now distributors of ethyl gasoline. Consumption of ethyl gas continues to increase, but greater attention is being given the anti-knock value of cracked gasolines. Cracked gasoline from Mid-Continent crude gives satisfactory results in engines of even higher compression than most 1928 motor cars. Brown has expressed the opinion that anti-knock value has been unduly emphasized and that ease of starting and acceleration are probably of greater importance. There is, however, an unmistakeable trend toward higher compressions. It is understood that the original plan of the General Motors Company and its subsidiary the Ethyl Gasoline Corporation, that the distribution of ethyl gas would have to be developed before any marked change could be made in engine compression. This has been accomplished *before* the distribution of really high compression engines.

MacCoul [25] has reported the results of a study of six motor fuels by ten co-operating laboratories, including the Anglo-Persian Oil Company, the Kansas City Testing Laboratories, the department of Chemical Engineering of the University of Michigan, Atlantic Refining Co., the Standard Oil Company of Indiana, the Texas Company, the Bureau of Standards, the Chrysler Corporation, the Tide Water Oil Company and the Mellon Institute. The principal object was to learn whether volatility affects the anti-knock values obtained with multi-cylinder engines more than it affects the values obtained from single-cylinder engines. The conclusions reached are :—

[25] *Oil and Gas J.*, May 10th, 1928, p. 208.

(1) Further refinement of anti-knock measurement is needed.

(2) Certain elements of technique, such as the mixture ratio and the spark setting should be standardized at once.

(3) Study of the methods used for the direct control of detonation in engine tests, such as the compression ratio and the manifold vacuum, should be made.

(4) Measurement of anti-knock value in terms of the mixtures of a reference fuel with benzol or tetra-ethyl lead is likely to be very misleading if the peculiarities of such scales are not well understood by the investigator.

(5) The data obtained indicate that probably no great difference in the results exists whether the detonation point is determined by durability, the maximum power, or the bouncing pin.

(6) The size and type of engine used does not seem to affect the results.

(7) A reference fuel of low anti-knock value and one of high anti-knock value should be standardized.

The results of another series of co-operative engine tests were described by Edgar,[26] in which the Armour Institute of Technology, the Atlantic Refining Company, Ethyl Gasoline Corporation, General Motors Corporation, Standard Oil Company of Indiana, Standard Oil Company of New Jersey, Universal Oil Products Company, University of Michigan and the U.S. Bureau of Standards participated. The gasolines compared included (1) a straight run gasoline from Mid-Continent crude, (2) a commercial aviation gasoline, (3) a straight run California gasoline, (4) a fuel made up of 70 per cent. of Number One and 30 per cent. benzol, and (5) Number One with 3·5 c.c. of pure tetra-ethyl lead per gallon. On the whole, the comparative ratings obtained by the different laboratories were in good agreement. A comparison of road test and bouncing pin methods of determining the quantity of tetra-ethyl lead needed for equating the fuels was also in very good agreement.

Reiman[27] has reported on a series of anti-knock measurements, using a Delco unit and expressing the results in terms of the percentage of aniline added to a paraffin base fuel serving as a standard,

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[26] *Oil and Gas J.*, February 2nd, 1928, p. 34.
[27] *Ind. Eng. Chem.*, 1927, **19**, 1055.

to equal the anti-knock value of the fuel under test. The following comparative results are of interest :—

TABLE 5.

Anti-Knock Value of Commercial Gasolines in Terms of Aniline Percentage.

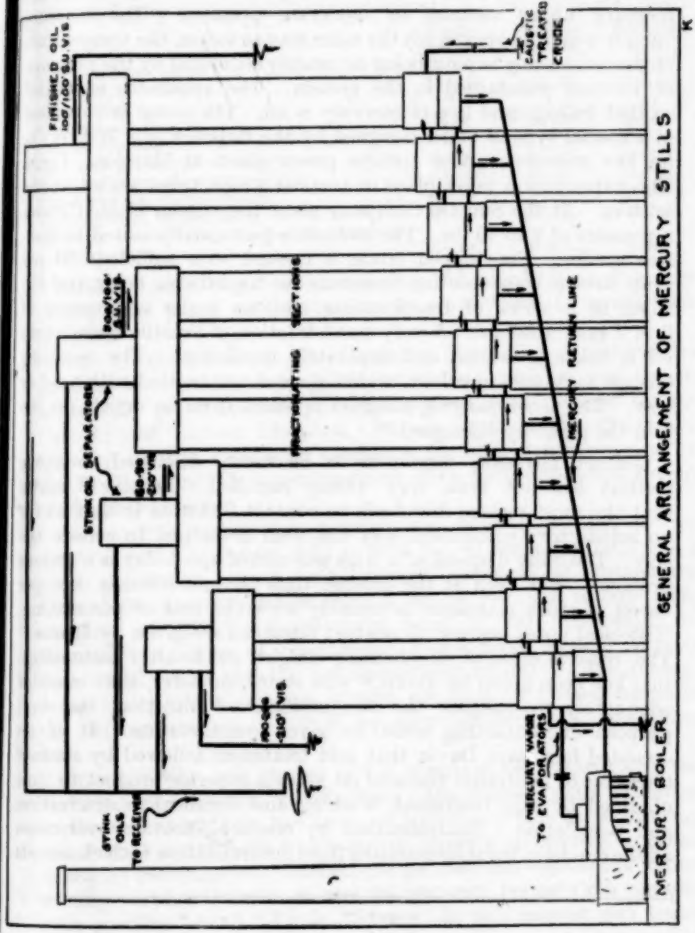
From paraffin base crude (Cabin Creek), 437° F. end-point	—0·50
From Mid-Continent crude, 437° F.	0·00
41% iso-octane + 59% n. heptane	0·00
Pressure cracked paraffin base, 437° F.	0·93
Pressure cracked, Mid-Continent, 437° F.	1·45
Vapour phase cracked, paraffin base, 437° F.	8·00
Pressure cracked, California, 410° F.	4·50
Mid-Continent + 3 c.c. tetra-ethyl lead	5·50
Pressure cracked, Mid-Continent, 400°F.	2·15
Pressure cracked, Mid-Continent, 375° F.	2·43
Mid-Continent, 10% casing-head	0·68
Mid-Continent, 25% casing head	1·03
Mid-Continent, 50% casing-head	1·98
Commercial premium anti-knock 1	3·75
Commercial premium anti-knock 2	3·75
Commerical premium anti-knock 3	3·42
Commercial ethyl gasoline 1	4·5 to 7·0
Commercial ethyl gasoline 2	4·5 to 5·5

LUBRICATING OILS.

The distillation of lubricating oils under a high vacuum continues to be more widely practised. Reciprocating feather valve vacuum pumps or steam jets and welded apparatus readily give the desired vacuum, but the more recent developments have had to do with the method of heating. Howard and Loomis [28] have applied the principal of flash distillation. They state, "In the distillation of a typical crude oil by methods common in the petroleum industry, practically three-fourths of the lubricating oil fractions are destroyed. A yield of 6 to 7 per cent. of an oil having a viscosity of 285 at 100° F. is commonly obtained from Mid-Continent crude. By the vacuum distillation of the same crude 24 per cent. of the same viscosity oil is readily obtainable." They also note that for an oil having an average molecular weight of 400, such as a Mid-Continent distillate of about 25° A.P.I. there is required 10 lbs. of steam per gallon of distillate to be equivalent to 1 inch or 25 mm. absolute pressure. Howard and Loomis started a commercial-sized vacuum pipe still in January, 1924. "To a great extent the advantages peculiar to vacuum pipe still equipment are those generally claimed for pipe stills operating at atmospheric pressure. Of special importance, however, are the advantages of uniform heating by maintenance of high velocity over the heating surface,

[28] *Nat. Petr. News*, December 14th, 1927, p. 28.

of reduced time during which the oil is subjected to heat, and particularly the advantage of lower temperature due to flash distillation."



Another solution of the heat input problem in connection with high vacuum distillation of lubricating oils is the use of mercury

vapour, which is being used on a large industrial scale by the Sun Oil Company. Since the boiling point of mercury at atmospheric pressure is 675° F., any temperature desired within the range from the upper limit of steam to 900° F. may be secured by boiling the mercury under vacuum or moderate pressure. The mercury vapour is used in very much the same way as steam, the temperature of the condensing vapour being accurately regulated by the pressure, or vacuum maintained in the system. The apparatus is welded so that leakage and loss of mercury is nil. The metal is vaporized in a special type of boiler designed by the Babcock and Wilcox Co. for the mercury vapour turbine power plant at Hartford, Conn. The vaporization takes place in vertical 4-inch tubes sealed at the bottom. At the Sun Oil Company plant the vapour is used under a pressure of 8 to 10 lbs. The method is particularly suited to wax-free crudes. The topped crude is treated with sufficient 50 per cent. caustic soda solution to retain the naphthenic acids and distilled in a series of fractionating sections under a pressure of 6 to 7 mm. absolute. A very small fraction of volatile malodorous oil is taken overhead and separately condensed. The resulting oils are very pale in colour, stable and are not treated with acid or clay. The accompanying diagram is taken from an article on the Sun Oil plant by Klemgard.[29]

Contact filtration continues to be much discussed, but the method has not been very widely installed. Lederer[30] states that the most serious drawback to contact filtration is that so far no satisfactory economical way has been developed to restore the clay. The daily disposal of a large amount of spent clay is a serious problem. But even at the present time contact filtering cost per barrel of stock compares favourably with the cost of percolating. Historical notes bearing on contact filtration are given by Bierce.[31] The relative costs of decolorizing bright stock after neutralization has been given by Davis,[32] who states, however, that in order adequately to compare the two methods of filtration, the dual purpose of contacting must be given consideration. It is an accepted fact, says Davis, that acid treatment followed by contact filtration to neutralize the acid oil gives a superior product to that obtained by acid treatment, washing and chemical neutralization and percolation. Neutralization by contact filtration overcomes all the emulsion troubles resulting from neutralization with chemicals

[29] *The Refiner*, February, 1928, p. 57.
[30] *Oil and Gas J.*, October 13th, 1927.
[31] *Nat. Petr. News*, December 14th, 1927, p. 101.
[32] *The Refiner*, March, 1928, p. 90.

and shortens and simplifies the treating operation. Davis gives the following comparison of cost :—

TABLE 6.

Relative Cost of Decolorizing Bright Stocks from ½ to 1 Tag.–Robinson Colour.

	Single contact.	Double contact.	Percolation.
Clay used, per barrel	44 lbs.	46 lbs.	133 lbs.
Clay cost, per ton	$14·00	$14.00	$20.00
Times used	1	1	40
Net cost per ton	14.00	14.00	0·50
Cost of burning	—	—	0·85
Clay cost per barrel of charge	0·308	0·322	0·090
Cost per barrel direct operation	0·050	0·196	0·270
Total cost per barrel charge	0·358	0·518	0·360
Yield finished bright stock	80%	98%	98%
Cost of decolorizing 1 barrel finished bright stock	0·448	0·528	0·367

So little has been published regarding the manufacture of greases that a brief paper on this subject by Cupi [33] will be noted with interest.

Natural-Gas Gasoline.—The fractional distillation of natural-gas gasoline to eliminate sharply the low boiling gases, is now almost universally practised. Patent infringement suits brought by the Carbide and Carbon Chemical Company against the Texas Co. and the Phillips Petroleum Company for alleged infringement of the De Brey and Thompson patents, have been decided in favour of the defendants.

Butane-free natural-gas gasoline has been advocated as an aviation fuel. It weighs 5·52 to 5·76 lbs. to the gallon and has a good anti-knock rating. The vapour pressures of butane-free natural-gas gasoline range from 8 to 14 lbs. per square inch, absolute, at 100° F., the average being 11 lbs. According to Oberfell,[34] a series of commercial motor fuels showed vapour pressure of 5·8 to 18·6 lbs. per square inch at 100° F., the average being 10 lbs. The addition of each per cent. of butane increases the vapour pressure at 100° F. by approximately ½ lb. per square inch.

Brown,[35] who has carried out a program of research for the Natural-Gas Gasoline Manufacturer Association, calls attention to the fact that there has been no laboratory test for measuring *volatility* of motor fuels which can be directly interpreted in terms of engine performance. Natural-gas gasoline has anti-knock values usually varying between 45 and 65 per cent. benzol (in a paraffin type gasoline blend). Little difference in this respect was found

[33] *The Refiner*, August, 1927, p. 55.
[34] *Nat. Petr. News*, May 23rd, 1928, p. 88.
[35] *Am. Inst. Chem. Eng.*, Preprint.

between natural gasolines from Eastern and Mid-Continent fields. By very extensive engine tests Brown has shown the value of natural-gas gasoline in blends, in case of starting and acceleration of the engine. In his opinion, as a result of these tests, U.S. motor gasoline is satisfactory for general service only in extremely warm weather, and gives the best performance in a warm engine only if the atmospheric temperature is above 70° F. According to Brown's tests, motor fuel for different seasons of the year should have the character shown by the following :—

TABLE 7.

Temperature at which the Indicated Percentage should be Distilled in the A.S.T.M. Distillation, Corrected for Loss and Residues.

Atmospheric temperature.	5–20%	30–50%	60–80%	90%
90° F.	200° F.	250° F.	350° F.	380–410° F.
60°	170°	215°	335°	380–410°
30°	140°	180°	320°	360–410°
0°	100°	150°	300°	340–410°

Lewis [36] discusses factors in the heat transmission of equipment in gasoline recovery plants and points out that condensation can take place on the cooled surface long before the gas as a whole has been cooled down to its dew point. In studying the heat transmission between a flowing mixture of steam and air, and a cooled pipe, a transmission coefficient was found which was "over tenfold what one would anticipate in view of the pipe diameter and gas velocity."

Possible uses for the propane and butane separated from natural-gas gasoline has been much discussed. It has been shown to be suitable for the enrichment of water gas, but its usefulness in this way has been prevented, in most localities, by economic factors, the chief of which is probably transportation cost. The gas-liquid relationships of these two hydrocarbons are as follows :—

	Propane.	Butane.
Cu. ft. of gas at 60° F. per gal. liquid	38·2	32·5
B.Th.U. per gallon of liquid	96,900	106,500
B.Th.U. per cu. ft. of gas at 60° F., 760 mm.	2,519	3,274

On a B.Th.U. basis it will accordingly be noted that about 10 gallons of liquid propane-butane are required to equal 1,000 cubic feet of lean natural gas. According to Burrell and Mase,[37] the use of propane-butane for gas enrichment is not promising. The trend of design in natural gasoline plants has been described by Campbell.[38] The largest natural-gas gasoline plant in the world is

[36] *Am. Inst. Chem. Eng.*, 1927, Preprint.
[37] *Nat. Petr. News*, January 4th, 1928, p. 67.
[38] *Nat. Petr. News*, September 1st, 1927, p. 45.

the recently completed No. 13 Plant of the Sinclair Co. Special tank cars have been designed for transporting liquid propane and butane, and approved by the I.C.C. These cars carry 30 welded containers, each container holding about 1,000 lbs. of the hydrocarbon.

Analytical.—Stevenson and Babor [39] consider that the dew point is the best indication of the temperature of complete vaporization, under equilibrium conditions of gasoline alone or mixed with air. Stevenson and Stark [40] developed their phase change method for determining the temperature of complete vaporization of gasoline at 760 min. under equilibrium conditions. This equilibrium end-point was called the Deppe end-point and was proposed as a substitute for the Engler distillation. Stevenson and Babor developed their present method to apply to air-fuel mixtures.

There has been some controversy over the percentage of sulphur permissible in motor fuel. Diggs [41] has published the result of a co-operative study by the Standard Oil Company of Indiana and the General Motors Company. A preliminary inquiry into a number of cases of bad wrist pin corrosion developed the fact that all of these motors had been operated on benzol or benzol blends. The corrosion developed mostly in cold weather. There was no evidence that appreciable corrosion occurred in warm weather, at least with continuous running of the engine. The corrosion was due to sulphuric acid. Diggs concludes that gasoline containing "0·151 per cent. sulphur does appreciable harm, and that 0·458 per cent. sulphur does very great harm." Mougey [42] also states that although the thermostats and ventilators are of very great value in combating corrosion, it is concluded that inasmuch as a large number of cars are not so equipped, an increase in the sulphur content of motor fuel is not in accord with the best interests of the automobile industry and the public. The U.S. Bureau of Mines recently reported that an examination of 130 commercial motor fuels only seven exceeded the 0·10 per cent. sulphur limit of U.S. motor specifications.

A rapid corrosion test, described by Rue,[43] consists in shaking 100 c.c. of the oil, with about 1 c.c. of mercury and filtering, the amount of corrosion being judged by the mercury sulphide precipitate on the paper. This test can be carried out in about two minutes. Faragher, Morrell and Monroe [44] have published a method for determining the types of sulphur present in a motor fuel. Hydrogen

[39] *Ind. Eng. Chem.*, 1927, **19**, 1361.
[40] *Ind. Eng. Chem.*, 1925, **17**, 679.
[41] *Ind. Eng. Chem.*, 1928, **20**, 16.
[42] *Ind. Eng. Chem.*, 1928, **20**, 18.
[43] *Oil and Gas J.*, May 10th, 1928, p. 162.
[44] *Ind. Eng. Chem.*, 1927, **19**, 1281.

sulphide is removed by cadmium chloride solution, sulphur by metallic mercury similar to the method of Ormandy and Craven (this Journal, 1923, 9, 135), mercaptans by alcoholic sodium plumbite and disulphides by reduction by zinc and acetic or hydrochloric acid. Kennedy [45] has described an improvement in the method of burning volatile fuels for sulphur determination which is used at the Bureau of Standards. A comparison of the Carius and the oxygen bomb methods for determining sulphur in heavy oils has been made by Devine and Lane,[46] who conclude that for routine work the oxygen bomb method is entirely adequate. The use of the much more tedious Carius method is necessary only when results of the highest accuracy are essential. The difference in the results by the two methods may amount to as much as 3 per cent. of the sulphur present.

Bailey [47] and his co-workers recommend the determination of nitrogen in petroleum oils by digesting 5 g. sample with 150 c.c. sulphuric acid, 50 g. potassium sulphate, 2·5 g. mercuric oxide and 2·5 g. copper sulphate. Bailey's figures for the organic nitrogen content of California oils are very much lower than the much quoted results of Maberry. Bailey finds that, contrary to the literature, the nitrogen compounds in neither crude petroleums nor distillates can be determined by extraction with dilute mineral acids.

In a study of transformer oils, Ford [48] found that unsaturation, as indicated by loss on treating with concentrated sulphuric acid, is roughly proportional to the rate of oxidation and sludge formation. Mead measured the oxygen absorbed and finds that the temperature coefficient per increase of 10° C. is 2·4 in the range 120–130° C. Sludge formation and development of acidity start very slowly, the rate increasing as oxidation progresses. Of 177 substances added to a transformer oil 48 showed a distinct inhibitory influence on sludge formation, of which three had a pronounced effect, i.e., sulphur, nitrobenzol and nitrocresol.

Miscellaneous.—Aluminium paint has been strongly advocated for painting storage tanks to reduce vapour losses. The U.S. Bureau of Mines, Report Serial 2,677, has reported the vaporization losses from a series of 55,000 barrel storage tanks containing 37·4° A.P.I. crude, and painted with aluminium paint, and a number of dark-coloured paints. Under conditions showing a loss of 1·24 per cent. for the black painted tanks, the aluminium painted tanks showed a loss of 0·83 per cent., a difference of 202 barrels.

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[45] *Ind. Eng. Chem.*, 1928, **20**, 201.
[46] *Oil and Gas J.*, May 17th, 1928, p. 164.
[47] *Ind. Eng. Chem.*, 1928, **20**, 83.
[48] *Ind. Eng. Chem.*, 1928, **19**, 1165.

Heat insulation problems of refineries are discussed by Rinehart.[49] The development of particular interest is the increasing use of hard asbestos-cement composition board, "Transite," instead of steel for outside insulation covering, for either high or low temperature insulation.

The heat of solution of paraffin wax has been determined by Sullivan, McGillard and French,[50] who finds that wax of 125°F. melting point has a heat solution of 40·3 Cal. per gram, or 72·5 B.Th.U. per lb. The same authors have determined the solubility of paraffin waxes of 111° F., 125° F. and 145° F. melting points, in petroleum ether, and in a number of Mid-Continent petroleum fractions of different viscosities. Rhodes, Mason and Sutton [51] have studied the crystallizing behaviour of slack wax and find, as has been shown by other recent investigations, that the relative amounts of needle and plate forms of crystals is determined by the conditions under which the crystallization is carried out.

Asphalt.—In spite of the increased use of concrete for road construction, it is of interest to note that the use of asphalt for this purpose continues to increase also. The production of petroleum residuum asphalt in 1927 was three and a half millions tons, not including road oils, an increase of about 16 per cent. over 1926. The ratio of asphalt used for paving purposes to all other uses remains about the same, i.e., about 55 per cent. Considerable notice has been given the enormous deposits of bituminous sands, carrying about 14 per cent. of bituminous matter, occurring along the Athabasca River in Canada. But no commercial development has as yet taken place. In Kentucky a bituminous sand suitable for road building, carrying 7 per cent. of bituminous matter, is quarried in commercial quantities.

Research.—While the larger and more progressive refining companies maintain research laboratories that would be a credit to any industry, it is interesting to note that according to a statistical average of the industry, the average American refinery represents a plant investment of $5,000,000, of which the laboratory represents $10,000.

Oklahoma State University, which provides courses in refinery technology under Prof. F. W. Padgett, has installed experimental refinery equipment capable of handling 300 barrels of crude per day. The equipment includes a 300 barrel pipe still, a 90 foot fractionating tower, and a 96 foot tower for studying gas and air lift conditions. The Bureau of Mines Experimental Station at

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[49] *Nat. Petr. News*, September 21st, 1927, p. 89.
[50] *Ind. Eng. Chem.*, 1927, **19**, 1040.
[51] *Ind. Eng. Chem.*, 1927, **19**, 935.

Bartlesville, Oklahoma, has also installed large-scale experimental equipment, including a tank 6 ft. by 60 ft., which is to be filled with sands from oil-producing strata for studying crude recovery problems. The Western Petroleum Refiners' Association has planned to support a co-operative research, primarily having to do with anti-knock gasoline.

Cracking.*

By GUSTAV EGLOFF, Ph.D., M.A., M.Am.Inst.Chem.E., M.Am.Chem.Soc. (Member) and C. D. LOWRY, Jr., M.Am.Chem.Soc.

1. INTRODUCTION.

DESPITE the tremendous over-production of crude oil during the year 1927, the amount of gasoline made by cracking increased. In the United States alone the cracking process yielded over one hundred million barrels of gasoline, or 31 per cent. of the total produced. This represented about 95 per cent. of the world's cracking of oil.

The year has seen a relatively rapid abandonment of pressure stills of the shell and water tube boiler type. Many cracking units of this character were shut down, one company alone writing off over two million dollars in obsolescence charges.

Improvement in the control of cracking has given flexibility of operation, allowing production of maximum yield of the product in greatest commercial demand, be it gasoline, kerosine, Diesel or furnace oil, residual fuel oil, incondensible gas or coke.

The average quality of gasoline marketed has distinctly improved, due largely to the fact that the cracking process gives gasoline higher in anti-knock value than that which is derived from the ordinary distillation of crude oil. A large proportion of the cracked gasoline produced is being sold at premium prices. Many coloured gasolines are also being marketed with marked success in the United States.

The increased production of crude oil has largely been of high sulphur content. This type of oil causes severe corrosion of equipment. High sulphur crude oils also bring about problems in the treatment of the cracked product. Technologic improvements have in large measure overcome the corrosion difficulties, and greatly improved the refining of the cracked gasoline. There is a distinct tendency in the States to increase the sulphur toleration in gasoline so as to reduce the loss of chemicals, and the loss of gasoline and its depreciation as to anti-knock properties due to treatment.

* Paper received June 18, 1928.

A re-awakened interest in vapour phase cracking, at atmospheric pressure, has developed, due to increased demand for high anti-knock gasoline. So far this type of operation has gone into but limited commercial use.

Some advance has been made in the scientific knowledge of cracking and the mechanism of its reactions. We are still in dismal ignorance, however, of the components present in cracking stocks, and have far from complete knowledge of the products derived therefrom.

2. Studies in the Mechanism of Cracking.

(*a*) *Thermal and Pressure Distillation.*

A number of scientific studies have been made under carefully controlled conditions, to find out what really goes on when oil is subjected to cracking conditions.

Sachanov and Tilitsheyew[1] have studied the cracking of a number of Russian oils to determine the effects of varying time, temperature, pressure, and charging stock. A 2½ litre autoclave was used, fitted with a dephlegmator and a condenser operating under pressure. In measuring the time rate of cracking, correction was made for the changes which took place while the oil was being brought to the cracking temperature.

From a Grosny paraffin base distillate cracked at 375–475° C. (707–887° F.) and 5 to 15 atmospheres pressure, the yield of gasoline (E.P. 200° C.—392° F.) increased with time to a maximum of 39 per cent., with 24 per cent. of kerosine (boiling 200° to 300° C. or 392° to 572° F.) produced at the same time. The total production of light oils (gasoline and kerosine) at a given temperature and pressure was a function of time, approaching a maximum which was the same for all the temperatures employed. The speed of reaction increased about six times for every 25° C. (45° F.) rise in temperature. The times required for maximum yields were as given in the table :—

375° C. (707° F.)	..	45 hours (estimated)
400° C. (752° F.)	..	9 ,,
425° C. (797° F.)	..	1½ ,,
450° C. (842° F.)	..	12 minutes
475° C. (887° F.)	..	2 ,,
500° C. (932° F.)	..	20 seconds.

[1] *J. Chim. Promys.* (Moscow), 1927, **4**, 516. *Petroleum*, 1927, **23**, 521. *Erdol Teer*, 1928, **4**, 9, 43. *Oil and Gas J.*, June 23, 1927, 144. *Ref. Nat. Gas. Manf.*, Oct., 1927, 84.

Gums, asphaltenes and coke formed in about the same amount at each temperature provided the time of heating did not exceed that required to produce maximum light oil yield. The gasoline contained 10 to 40 per cent. unsaturates, the proportion being reduced by increased pressure, though the authors believe this effect might be absent in tube stills.

Paraffin, paraffin base distillate and white vaseline oils gave somewhat higher yields of light oils and much less gum, asphaltenes and carboids, while heavy crudes and fuel oils gave less gasoline and more coke. From this it was deduced that the condensation products were formed from hydrocarbons of other than the paraffin series, probably aromatic compounds.

Except for gas oil and kerosine distillate the various stocks cracked with about equal ease. Roughly, gas oil cracked twice as slowly as the heavier fractions and kerosine distillate five times as slowly as gas oil. Cracking of paraffinic oils gave gasoline composed almost entirely of paraffin and olefine hydrocarbons, while other stocks produced some naphthenes. From this the conclusion was drawn that the naphthenes in cracked products are not formed by condensation of olefinic substances, but from cyclic compounds originally present in the charging stock.

Waterman and Perquin[2] have reported detailed investigations of the products of cracking of Rangoon paraffin with and without the use of hydrogen. The cracking itself was reported in an earlier paper.[3] The material boiling below 150° C. (302° F.) was separated first into 10° then into 5°, 2° and 1° C. fractions. The distillation curves of the spirits from the two processes differed little, there being in both curves peaks indicating the presence of pentane, hexane, heptane and octane each to the amount of 3 to 4 per cent. in the Berginized (hydrogenated) spirit and somewhat less in the cracked spirit. The refraction, dispersion, aniline number and bromine number of the distillates were measured. The Berginized fractions (as well as the residues from distillation) were but slightly unsaturated and were relatively stable, as even after 12 to 18 months they showed no change ; while the cracked material was much more unsaturated and changed rapidly on standing. As the boiling points of the respective fractions increased the differences between the distillates from the two processes augmented, while there were indications of other than aliphatic hydrocarbons in the distillate from cracking.

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[2] *Rec. trav. Chim.*, 1927, **46**, 813. *Bull Soc. Chim. Ind.*, 7th Congress of Industrial Chemistry, 1927. *J. Inst. Petr. Techn.*, 1927, **13**, 413.
[3] *Rec. trav. Chim.*, 1926, **45**, 284.

Brame and Hunter[4] analysed the distillate made by cracking Russian oil. The crude material had the following characteristics :—

Specific Gravity	0·751
Aniline Point	40·0° C. (104° F.)
Unsaturates	27·20% (by loss to 85% sulphuric acid)
Aromatics	4·97%
Saturated Compounds (by difference)	67·83%

The fraction boiling below 120° C. (248° F) was refractionated and the physical properties and chemical constitution of each cut determined. Olefines were separated by bromination and distillation, and recovered by treatment with the zinc-copper couple, the cyclic olefines and diolefines then being removed from the unsaturated fraction with mercuric acetate. Aromatic compounds were taken out with 98 per cent. sulphuric acid and the naphthenes eliminated with nitric acid. In brief, their findings in the various hydrocarbon groups were as follows :

Paraffins.—Hexane, heptane and the isohexanes trimethyl ethyl methane and di-isopropyl were identified. There were indications of pentane, isopentanes and isoheptanes.

Naphthenes.—Methyl pentamethylene, hexamethylene, di-methyl pentamethylene, and methyl hexamethylene were isolated, but pentamethylene could not be detected.

Olefines predominated in the lower fractions. The type $RCH{=}CH_2$ appeared to be absent ; 3 and 2 methyl pentene and 4 and 5 methyl hexene were probably present.

Diolefines were indicated in the first fractions with definite evidence of piperylene.

Cyclic olefines predominated in the unsaturated compounds boiling from 90° to 120° C. (194–248° F.).

Aromatics, assumed to be benzene and toluene, were present in small percentages.

K. Kostrin [5] cracked at rather low pressure. He stated that in the past high pressures had been used in order to reduce the unsaturated content of the gasoline. Since it is now known that the unsaturated compounds have high anti-knock value, the tendency is towards a reduction in pressure. Paraffin fuel oil from Surachani was decomposed at 480°–490° C. (896–914° F.) and 2½ to 3 atmospheres pressure into 33·5 per cent. distillate and 59·2 per cent. residue. The latter solidified 12° lower than the charging stock and was well suited for fuel oil use. The distillate began to boil at 39° C. (102° F.) and 39 per cent. went over up to 150° C. (302° F.).

[4] *J. Inst. Petr., Techn.* 1927, **13**, 794.
[5] *Neftjanoe Choz.*, **12**, 39. *Chem. Zentr.*, 1927, II, 1523.

The gasoline so obtained contained 13 per cent. of unsaturated hydrocarbons, a figure which treatment with Florida earth reduced to 6½ per cent. through polymerization, the upper boiling limit being raised at the same time. Sulphuric acid had a similar but more pronounced action and for this reason was not recommended as a refining agent.

(b) Cracking with Catalysts.

Graetz [6] made an extended investigation of the cracking of petroleum with aluminium chloride and other metallic halides. Dehydrated and refined Gabian petroleum gave increasing yields of light oils boiling to 210° C. (410° F.) with increasing proportions of aluminium chloride until a maximum of 74·5 per cent. spirit was reached with 9 per cent. of the reagent.

Stannic, mercuric, cupric, ferric, sodium and sulphur chlorides and bleaching powder formed complexes with the oil. It was stated that in order for cracking to be catalysed by a metal chloride, the halide must be volatilized or decomposed between 190° C. and 210° C. (374–410° F.); apparently at the distillation or decomposition temperature of the chloride the hydrocarbon metal chloride complex is broken down, with the breaking of the carbon chain and formation of lower boiling oils. The minimum cracking temperature was given as 160° C. (320° F.) with the reaction well started at 200° C. (392° F.); complexes formed by sulphur and stannic chlorides were not useful because they decomposed before the minimum cracking temperature was reached, while those of the high boiling chlorides, as ferric chloride, were so stable that cracking could not begin before 250–260° C. (482–500° F.). The decomposition of the aluminium chloride complex at atmospheric pressure began at 150–160° C. (302–320° F.), was fairly active at 190–210° C. (374–410° F.), and complete at 230–240° C. (446–464° F.). It was suggested therefore that it would be best to carry out cracking with aluminium chloride at 240–245° C. (464–473° F.).

Koboyashi and Yahamoto [7] find that Japanese acid clay has a cracking effect on heavy oils which they compare to that of pressure. No gasoline cut was taken, but the fraction boiling to 150° C. (302° F.) from gas oil and heavy California oils amounted to about 10 per cent.

Gault and Sigwalt [8] have continued their earlier work on the cracking of hexadecane, working in the gas phase and cracking both in an empty quartz tube, and in the same tube packed with catalysts.

[6] *Ann. Office Nat. Comb. Liquides*, 1927, **2**, 69.
[7] *J. Soc. Chem. Ind.*, Japan, 1927, **30**, 17 B. *Brennstoff Chemie*, 1927, **8**, 329. *Petr. Times*, 1928, **19**, 218.
[8] *Ann. Office Nat. Comb. Liquides*, 1927, **2**, 309, 543.

These catalysts included grains of quartz, and pumice coated with carbon or reduced nickel. Cracking experiments were also made in the liquid phase with aluminium trichloride. The results obtained indicated that cracking temperatures could be considerably lowered by the use of quartz or pumice, but that the final products then differed from those obtained with an empty tube. Aromatic hydrocarbons were believed to be produced from the lower ethylenes, which were the primary products of the degradation, and not from acetylene, which was not present in the gaseous products.

In the absence of chemical catalysts, at low temperatures the carbon chain appeared to break indifferently at any point, but as the temperature increased the fission tended to approach the terminal carbons. Substances such as nickel brought about deep-seated decomposition. When they were not used, differences in the liquid hydrocarbons obtained were due to secondary reactions, for the primary products at various temperatures appeared to be essentially the same, though changing readily. Carbon-coated pumice was less active at 400–450° C. (752–842° F.) than pumice alone. The gaseous products, with nickel, consisted of hydrogen and methane, while the liquid products, few in number, consisted of aromatic and naphthenic hydrocarbons. The liquid phase cracking of hexadecane with aluminium chloride gave chiefly butane and a little propane with small amounts of other substances.

Bowen and Nash,[9] by the passage of toluene or petroleum fractions containing toluene over aluminium grains covered with vanadium oxide at 400° C. (752° F.), produced traces of anthraquinone, benzoic acid and benzaldehyde.

Szanyna[10] described experiments on the cracking of Boryslaw gas oil. In simple cracking by the application of heat, the gasoline yield reached a maximum of 27 per cent., as against yields from the Bergius process of 46 per cent. and of 44 per cent. in cracking with aluminium chloride. With increasing temperature the density of both the gasoline and the residue increased. The proportion of unsaturated hydrocarbons in the distillate remained almost unchanged, while that of aromatics rose and that of saturated hydrocarbons decreased. Among the saturates the naphthenes disappeared and the proportion of paraffins grew. Increasing pressure did not influence the gasoline yield, but increased its saturation. With high pressure in the Bergius process hydrogen was absorbed. As cracking catalysts, aluminium chloride was active, while carbon and nickel were not. In tubes of different materials the optimal temperature increased in the order of their heat conductance—copper, iron and quartz.

[9] *Nature*, 1927, **120**, 621.
[10] *Prz. Chem.*, **11**, 451. *Chem. Zentr.*, 1927, **II**, 996.

Dobrjanski and Murejewa [11] discuss cracking in the liquid phase, using atmospheric pressure and a temperature of 405–415° C. (761–779° F.) with machine oil, cylinder oil and paraffin as charging stock. The amount of ethylene and heavy hydrocarbons produced decreased as decomposition went on, while the saturated hydrocarbons increased. Possibly in the first stages of decomposition the large side chains of aromatic hydrocarbons were broken down after which further change occurred leading to saturated bodies. With increase in the extent of cracking the liquid distillate grew denser and its content of material boiling below 150° C. (302° F.) decreased. The reaction was not affected by pumice, coke, copper or iron turnings.

3. Liquid Vapour Phase Cracking.

(*a*) *Operation of Cracking Systems.*

A number of descriptions of commercial cracking processes and their operation in various refineries have appeared during the past year.

The Richey [12] system, a "liquid phase process of the tube and tank kind," passes the charging stock through a heating coil, a soaking coil and heat interchangers at a pressure of 600 lbs. The pressure is reduced with consequent vaporization of the oil. A yield of 30 per cent. gasoline and 50 per cent. recycle stock is claimed.

The Blümner Process[12a] treats oil in an autoclave, containing molten lead, maintained at 850° F. (454° C.) under a pressure of 35 to 40 atmospheres. Yields of 25 to 50 per cent. of motor fuel are reported, depending on the stock cracked.

The Derby Oil Co.[13] operates its four Dubbs units with the flashing system. Residuum from the reaction chamber is fed to a drum, the vapours from which mix with fresh charging stock, while the liquid residue is a high grade fuel oil. It is stated that the gasoline yield is a little higher than on the older method of operation, and its anti-knock value is greater, while other advantages are lengthened period of operation, lowered coke formation and greatly increased capacity of the plant.

In the operation of Dubbs cracking units at the Vickers Petroleum Co.[14] the formation of coke has been reduced from

[11] *Neftjanoe Choz.*, **12**, 411. *Chem. Zentr.*, 1927, II, 1524.
[12] *Oil and Gas J.*, Feb. 17, 1927, 158.
[12a] Salmony, Erdöl Teer, 1928, **4**, 31. Karsten, Petroleum, 1928, **24**, 423. *Petr. Times*, 1928, **19**, 579.
[13] *Oil and Gas J.*, April 12, 1928, p. 140.
[14] *Nat. Petr. News*, August 3, 1927, 83.

approximately 30 lbs. per barrel of charging stock to 5 lbs., with a marketable residual oil passing all specifications. An increase in the period of operation of the units of from 4 to 22 days has been achieved, with a yield of over 53 per cent. gasoline, based on the charging stock.

The Marland Refining Company [15] operates Fleming, Cross and Dubbs units. The Fleming units make about 33 per cent. gasoline from gas oil, operating at 100 lbs. pressure. The Cross plant operates at between 650 and 700 lbs., using 50 per cent. gas oil and 50 per cent. recycle stock, and yielding 29 per cent. gasoline on the basis of the oil treated. The Dubbs units operate on fuel oil and heavy stocks using 200 lbs. pressure. The yield of finished gasoline is 60 to 62 per cent. of the cracking charge. Gray vapour phase treating towers are hooked to the bubble towers of the re-run stills. Lime is fed in with the charging stock to check corrosion.

The Paragon Refining Co.[16] has remodelled its plant and added Dubbs cracking units. Bottoms from the crude battery while still in a heated condition are fed directly to the cracking stills and produce 80 per cent. pressure distillate, 10 per cent. gas oil, and 10 per cent. coke and gas. The yield of gasoline is 58 per cent. of the cracking stock.

In the operation of Holmes-Manley stills at the Lincoln Oil Refining Co.[17] the oil passes through coils in a furnace, attaining a temperature of 850° F. (454° C.) under 350 lbs. pressure, and then to four gas-heated stills, equipped with scrapers. The tar passes to a flash tank. The gasoline is scrubbed with 30° A.P.I. caustic soda, is sprayed into a fractionating tower and passes to a still heated by steam to 200° F. (93° C.). It is given a doctor treat but no acid is used.

The Simms Oil Co.[18] secures a 40 per cent. gasoline yield by cracking Smackover crude in both a tube still and Cross units. The tube coil is operated at a temperature of 830–850° F. (443–454° C.) and 150 lbs. pressure, the pressure being reduced as the oil enters an evaporator, from which the vapours enter a bubble tower. Fifteen per cent. of naphtha is taken off overhead, and the gas oil collected for charging to the Cross units.

The Panhandle Refining Co.,[19] by use of a heating coil maintained at a temperature of abour 840° F. (449° C.) and a pressure of 175 lbs., produce 10 per cent. of gasoline due to cracking during the reduction

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[15] *Nat. Petr. News*, April 25, 1928, 85.
[16] *Nat. Petr. News*, Jan. 25, 1928, 23.
[17] *Nat. Petr. News*, June 29, 1927, 25.
[18] *Ref. Nat. Gas. Manf.*, April, 1928, 60.
[19] *Oil and Gas J.*, Jan. 27, 1927, 32. *Ref. Nat. Gas. Manf.*, Mar., 1927, 55.

of the topped crude, thus lessening the volume of material to be put through the primary cracking stills.

The Louisiana Oil Refining Corp.[20] blends its cracking stocks to produce a charging stock of uniform quality and ready conversion into gasoline. The cracking units are of the "tube and tank type." Oil at 450° F. (232° C.) is charged to the cracking coil, where it reaches a temperature of 850° F. (454° C.) under 300 lbs. pressure. The vapours are fractionated by refluxing against the incoming oil.

Kauffman[21] describes an installation at the Parco, Wyo., refinery of the Producers and Refiners Corp., of a cable device to break up the coke in Dubbs reaction chambers and a conveyor passing it to storage.

Williams[22] discusses the plant of the Crystal Oil Refining Corp., at Shreveport, La., which includes two Jenkins units operating up to 300 lbs. pressure and 1,165° F. (630° C.) giving about 35 per cent. of gasoline based on oil charged.

Reid[23] takes up the operation of the plant of the Root Refineries Inc., which uses the Dubbs cracking process. Fourteen per cent. gasoline is obtained from Smackover crude oil by ordinary distillation, and an additional 38 per cent. by cracking.

The Johnson Oil Refining Co.[24] operates Dubbs units from which the cracked naphtha is acid treated, neutralized, and re-run and the gasoline mixed with straight-run product and gasoline absorbed from still gases before a final doctor treatment is given.

The Bell Oil and Gas Co.[25] has in operation a modern pipe still and a Dubbs cracking unit.

Full descriptions of the construction and operation of Cross[26] and Jenkins[27] units and a historical sketch of the Burton process[28] have also appeared.

Sedlaczek[29] has described a number of cracking processes.

Numerous articles written from a practical point of view concerning the handling of cracking units have appeared in the oil journals. In a series of three papers, Gerstenberger[30] takes up

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[20] Reid, *Ref. Nat. Gas. Manf.*, Jan., 1928, 56.
[21] *Oil and Gas J.*, Sept. 22, 1927, 206.
[22] *Oil and Gas J.*, August 18, 1927, 142.
[23] *Ref. Nat. Gas. Manf.*, Feb., 1928, 69.
[24] Reid, *Ref. Nat. Gas. Manf.*, Feb., 1928, 78.
[25] Goode, *Ref. Nat. Gas. Manf.*, March, 1927, 59.
[26] Rogers, *Petr. Times*, 1927, **18**, 539, 589.
[27] Willson, *Oil and Gas J.*, Dec. 1, 1927, J1.
[28] Humphreys, *Oil and Gas J.*, June 2, 1927, 154.
[29] *Teer*, 1927, **25**, 245, 332, 418.
[30] *Nat. Petr. News*, July 27, 1927, 71; August 17, 1927, 69; August 31, 69.

the operation of pressure stills and the variations that must be made for different crudes. He advises running for high throughput rather than maximum gasoline yield, and stresses the importance of proper maintenance of temperature, efficient fractionation and keeping up the temperature of the oil entering the unit.

Kauffman has discussed the inspection of cracking equipment to follow its deterioration.[31] Beatte[32] gives rules for safety in cracking unit operation, while Chatfield[33] describes means of handling Dubbs residue as fuel. Papers have also appeared on the various types of hot oil pumps for cracking units,[34] and on the manufacture and testing of reaction chambers.[35]

Conditions during the past year brought out discussion of the profit-making possibilities of cracking, not only with regard to the United States,[36] but also as affecting France[37] and Rumania.[38] There have also appeared a number of résumés of recent developments in cracking,[39] notably a summary by Singer.[40]

(*b*) *Cracking of Individual Oils.*

Studies of the behaviour of different cracking stocks when subjected to cracking conditions are of import.

Egloff and Morrell[41] cracked Seminole topped crude oil at 830–850° F. (443–454° C.) and 135 lbs. pressure. On a non-residuum basis 67·4 per cent. of gasoline was produced, on a residuum basis 53·7 per cent. and by combined topping and cracking 79·8 per cent. and 77·1 per cent. respectively. The cracked distillate was readily refined with sulphuric acid, water and plumbite, followed by a fire and steam distillation and a dilute caustic wash. The cracked gasoline was equivalent in anti-knock value to a 25 per cent. benzol blend with Pennsylvania straight-run gasoline.

The same authors[42] topped and cracked both a heavy and a light Spindletop crude oil, and refined the distillates produced.

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[31] Kauffman, *Ref. Nat. Gas. Manf.*, July, 1927, 59.
[32] *Nat. Petr. News*, March 28, 1928, 87.
[33] *Nat. Petr. News*, Jan. 26, 1927, 29.
[34] *Nat. Petr. News*, Sept. 21, 1927, 59.
[35] Rockefeller, *Ref. Nat. Gas. Manfr.*, March, 1928, 96. Haupt, *Nat. Petr. News*, Nov. 23, 1927, 61.
[36] *Oil and Gas J.*, 1927, March 31, 36; April 7, 167; May 12, 157; July 28, 158.
[37] *Chimie et Industrie*, Special No. 239, May, 1927.
[38] *Rev. Petrolifere*, Jan. 29, 1927, 14.
[39] Florentin, *Bull. de la Soc. de Chim. Indust.*, Seventh Congress of Industrial Chemistry, 1927; Sachs, *Rev. Petrolifere*, Nov. 19, 1927, 13; Nov. 26, 1927, 19.
[40] *Petroleum*, 1927, **23**, 1141; 1928, **24**, 175.
[41] *Nat. Petr. News*, June 1, 1927, 56. *Oil and Gas J.*, May 19, 1927, 152 *Petroleum*, 1928, **24**, 23.
[42] *Petroleum*, 1927, **23**, 898. *Oil and Gas J.*, April 14, 1927, 156, 159.

The heavy oil (24·1° A.P.I.) was cracked on a non-residuum basis at 840° F. (449° C.) and 150 lbs. pressure, yielding 58·1 per cent. Navy end-point gasoline. On a residuum basis at 810° F. (433° C.) and 150 lbs., 46·1 per cent. gasoline was obtained. The distillate was treated with acid and plumbite and distilled, using steam. The light crude, 28·7° A.P.I. cracked under the same conditions, gave on a non-residuum basis 65·2 per cent. gasoline and on a residuum basis 52·9 per cent. The distillates were treated as were those from the heavy oil. Both gasolines were of high anti-knock value, equivalent to a 45–50 per cent. benzol blend with Pennsylvania straight-run gasoline.

In a further study[43] they obtained 31 per cent. gasoline by topping Ventura crude oil, and then cracked the topped oil. In non-residuum operation at 810°—860° F. (432°—460° C.) and 125 lbs. pressure, 57·2 per cent. gasoline was obtained, based on the topped crude, and on residuum operation 48 per cent. The cracked distillates, containing 0·68 per cent. sulphur, were refined by washing with 16° Be. caustic soda and water, treating with sulphuric acid, neutralising with plumbite, washing with water, and steam and fire distillation. The gasoline was then water white, stable, sweet and non-corrosive and contained 0·27 per cent. sulphur.

Heinze[44] cracked gas oil and residuum from Hanover petroleum by the Dubbs' process at pressures of 14, 17 and 21 atmospheres on the gas oil, and 5 atmospheres on the residuum. He reported maximum yields of 40 per cent. motor fuel from the gas oil and 30 per cent. from the residuum. The gasoline contained 23 per cent. of aromatic compounds, and had a benzol equivalent of 21 per cent.

He also described[45] the small scale cracking of Halle paraffin oil from brown coal by the Dubbs' process, obtaining 29 to 33 per cent. refined gasoline. This was treated by washing with alkali, acid, doctor solution and water. In anti-knock value it was equivalent to a 25 per cent. benzol blend of Mid-Continent straight run gasoline.

Kogerman[46] cracked Estonian shale-oil on a non-residuum basis to 38·7 per cent. gasoline.

Roy Cross[47] described the cracking of shale-oil at 850° F. (454° C.) and 1000 lbs. pressure and the treatment of the gasoline produced. From 50 to 82 per cent. of gasoline was obtained, depending on the gravity of the initial oil. As treating losses with concentrated

[43] *Nat. Petr. News*, August 10, 1927, 76. *Petroleum*, 1928, **24**, 145. *Oil and Gas J.*, July 14, 1927, 130.
[44] *Petroleum*, 1928, **24**, 237.
[45] *Petroleum*, 1927, **23**, 1169.
[46] *Petr. Times*, 1927, **18**, 903.
[47] *Oil and Gas J.*, March 10, 1927, 96, 148, 151.

sulphuric acid would be very high, brief treatment with dilute acid was recommended, followed by clay and caustic soda or doctor if desired to remove cresols. A second method that would be applicable is the use of earth or clay, which has been treated with copper, the hydrocarbons being treated in the vapour phase. Metallic sodium might also be used. The gasoline had a 40 per cent. benzol equivalent.

Gault and Stemart[48] cracked crude oil and gas oil from Autun shale, obtaining maximum yields of gasoline at about 600° C (1112° F.), with the crude oil and at about 650° C. (1202° F.) with the gas oil. Weiderpass[49] partly transformed the oil from Estonian shale or a distillate therefrom into aromatic compounds by cracking. The operating conditions were best at 750° C. (1382° F.). The content of identifiable aromatics rose from 23 to 36·5 per cent.

Pyhala[50] obtained 21 per cent. of light oil in the gasification of Russian petroleum by the Pintsch process, the oil being made up of aromatic hydrocarbons. Aschan[51] decomposed Russian fuel oil at 700°—800° C. (1292°—1472° F.) to obtain isoprene, benzene and toluene. Zakharenko and Mistchenko[52] found that fuel oil containing some water white oil was not suitable for cracking under atmospheric pressure. The rate of cracking doubled with every 10° C. (18° F.) rise in temperature.

Varga and Erdely[53] have made a laboratory comparison of the cracking of Texas, Grosny (Russian) and Moreni (Rumanian) gas oil and several crude and refined lignite tars. Pressures of 10 to 30 atmospheres and temperatures of 390°—450° C. (734°—842° F.) were used. At about 440° C. (824° F.), the Russian oil gave a maximum of 57 per cent. gasoline (to 200° C. or 392° F.) and the Texas and Rumanian oils about 45 per cent. The refined tars gave 32 to 37 per cent. light spirit, and the unrefined tars a 28 to 32 per cent. yield, at a temperature of about 420° C. (788° F.).

Dunstan and Shatwell[54] cracked residuums and distillates from two low temperature coal tars on a small scale at pressures of 160 to 550 pounds and temperatures of 440° C.—450° C. (824°—842° F.) obtaining 7½ to 12 per cent. of motor spirit, high in tar acids. The spirit was not difficult to refine and had a benzol equivalent of 40 to 50 per cent.

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[48] *Ann. Off. Nat. Comb. Liq.*, 1926, 305. *Chimie et Industrie*, 1927, **17**, 402.
[49] *Sitzungsber d. Naturforscher Ges. bei d. Univ. Tartu*, **34**, 2. *Chem. Zentr.*, 1927, II., 2027.
[50] *Erdol Teer*, 1927, **3**, 43, 58.
[51] *Chem. Ztg.*, 1927, **51**, 4.
[52] *Azerbeidj Neft. Khoz.*, 1927, No. 4, 42. *Chem. Abs.*, 1927, **21**, 3738.
[53] *Brennstoff Chemie*, 1927, **8**, 133.
[54] *Ind. Chemist*, 1928, IV., 109.

Cracking of Individual Oils.

U.S. Patents.

Roy Cross (U.S.P. 1,631,401, June 7, 1927) discloses "a process of making motor fuel having anti-detonating properties, comprising the steps of subjecting petroleum oil to the solvent action of sulphur dioxide, removing the undissolved hydrocarbons from the sulphur dioxide fraction, extracting the sulphur dioxide from the dissolved fraction and subjecting the residue to cracking conditions of temperature and pressure."

Lazar Edeleanu (U.S.P. 1,661,565, March 6, 1928) has developed an improved success for the cracking of hydrocarbons, which consists in submitting to a pressure cracking process that portion of petroleum distillates which remains undissolved after being treated with liquid. sulphur dioxide. The value of this treatment is shown by the following table from the patent specification :—

	Non-treated gas oil. Per cent.		Treated gas oil Per cent.
Cracked distillate	82	..	90·5
Gasoline	45	..	53·7
Coke	4·6	..	1·5
Sulphur in the cracked distillate ..	0·34	..	0·09
Sulphur in gasoline	0·1	..	0·06

Canadian Patent.

Clarence I. Robinson (Can. P. 268,753, March 1, 1927) cracks paraffin at a temperature of 700°–735° F. (371°–391° C.) and a pressure not exceeding sixty pounds, treats the distillate with sulphuric acid and then distils it, to obtain fractions of desired boiling points; one product specified has a distillation range of 300°–575° F. (149°–302° C.).

(*c*) Patents Covering Liquid-Vapor Phase Cracking.

U.S. Patents.

H. H. Armstrong (U.S.P. 1,613,010, Jan. 4, 1927) heats oil under pressure, and expands the same in the presence of super-heated steam and gas under a reduced pressure. For example, oil at 700° F. (371° C.) may be with super-heated gas maintained at approximately 1300° F. (704° C.) and the mixture subjected to pressure below atmospheric.

O. Behimer (U.S.P. Reissue 16,887, Feb. 14, 1928) discloses a process in which substantially all the cracking occurs in a vessel to which no external heat is applied except as necessary to compensate for heat losses. The oil prior to its introduction into this vessel is subjected to a high degree of cracking heat, and the excess heat of the oil is used to effect its decomposition.

W. Brink (U.S.P. 1,652,344, Dec. 13, 1927) subjects oil to cracking conditions in a chamber, the liquid and vapours impinging upon a baffle plate, the liquid portion passing to the bottom of the expansion chamber, and flowing back into the cracking still, which is maintained under temperatures ranging from 475° F. (246° C.) to in excess of 1000° F. (538° C.) and pressure approximating fifty pounds.

H. W. Camp (U.S.P. 1,657,524, Jan. 31, 1928) claims a process and apparatus for heating hydrocarbon oils and controlling the dephlegmation of the vapours by means of cooling the reflux condensate and injecting it into the dephlegmator in controlled portions. A portion of the cooled reflux may be injected into the cracking portion of the system.

J. R. Carringer (U.S.P. 1,656,724, Jan. 17, 1928) presents as an improved cracking apparatus "the combination of a heating conduit, a digesting or cracking passageway having provision against material temperature loss, a connecting line from said heating conduit to the digesting passageway, an air cooled tower on said connecting line, dampers for regulating the air flow in said tower, and a vapour separator for receiving products from the digesting passageway."

Roy Cross (U.S.P. 1,624,778, April 12, 1927) subjects oil to high temperature and pressure conditions, utilising the cracked residue and vapours as a means of heat interchange with the oil to be converted. The oil undergoing treatment is subjected to turbulence. It is claimed that by means of a scraper device actuated by the residue oil leaving the reaction chamber, carbon deposition in the reaction chamber is prevented.

W. M. Cross (U.S.P. 1,624,889, April 12, 1927) claims a process of converting hydrocarbon oils, which comprises heating and digesting the oil in a coil and enlarged chamber to the extent that the oil attains a substantial equilibrium prior to the withdrawal of the products of conversion, maintaining a body of liquid oil in the enlarged chamber under the pressure of gases and vapours evolved from the oil, and withdrawing products of conversion from the enlarged chamber. The conditions of cracking are given as a temperature between 750° F. to 1000° F. (399–538° C.), and superatmospheric pressure.

W. M. Cross (U.S.P. 1,643,446, Sept. 27, 1927) presents "a process for treating petroleum hydrocarbons comprising raising the oil to a cracking temperature in a heating stage, collecting all the oil to be treated in a reaction stage while maintaining temperature and pressure conditions adapted to effect conversion while the oil is substantially in the liquid phase, withdrawing all the conversion products from the reaction stage in a relatively small stream, releasing the pressure on the stream and injecting steam into the flowing stream, admitting the mixture of oil and steam to an enlarged zone maintained at reduced pressure to distil off the lighter fractions of the converted products." The conditions of cracking are given as a temperature from 750° F. to 1000° F. (399–538° C.) under pressure.

W. M. Cross (U.S.P. 1,644,991, Oct. 11, 1927) gives cracking conditions under his patent as normally ranging from 600° F. to 1000° F. (316–538° C.) and pressures from 400 to 1000 pounds. He claims "a process for converting oil comprising raising the oil to a cracking temperature in a heating stage, passing the oil to a conversion stage and there maintaining it under sufficient pressure imposed by the generated vapours during reaction to maintain the oil in substantially the liquid phase, relieving the pressure on the oil and passing it through a vaporizing stage, and there separating the liquid and vaporous oil constituents, subjecting the vapours evolved to a fractional condensing action, and returning selected portions of the condensate to the heating stage and to the fractional condensing stage with the charging stock, and maintaining a regulated liquid level in the vaporizing and fractional condensing stages."

W. M. Cross (U.S.P. 1,666,119, April 17, 1928) presents a process of treating petroleum hydrocarbons, "comprising the steps of heating the oil in a preliminary heating stage to a temperature to vaporize the lighter hydrocarbons, passing said heated oil to a vaporizing stage and there separating the liquid and volatilized material, returning the liquid products for further heating to vaporize additional fractions of higher boiling point, and passing the reheated material to a separate vaporizing stage, and controlling the relative heating to which the charging stock and re-cycled stock are subjected by limiting the extent of their circulation through the heating zone."

W. M. Cross (U.S.P. 1,667,883, May 1, 1928) claims "a process for treating hydrocarbon oil consisting in fractionally distilling the oil, condensing and separately collecting the respective fractions, withdrawing the tarry residual products, subjecting the gasoline-like fractions to a refining action and redistillation to produce refined gasoline, directing the more refractory fractions and selected portions of the residual material to a cracking stage, and there subjecting said fractions and residual material to a conversion temperature and pressure in excess of 500 pounds, whereby the conversion is effected substantially in the liquid phase, drawing off the synthetic product containing a substantial percentage of low boiling oils and cooling it, returning said product to be recycled through the fractional distillation stage and diverting a portion of the heavy residual oils from the system."

W. F. Downs (U.S.P. 1,616,079, Feb. 1, 1927) has designed a still which may be used for vaporization or for cracking under pressure in which a horizontal plate and a vertical partition increase convection in the oil being heated and release vapours from a large surface.

C. P. Dubbs (U.S.P. 1,627,159, May 3, 1927) claims "a process for converting petroleum into lower boiling point hydrocarbons, consisting in collecting the oil in a plurality of pools and while under pressure, subjecting the pools of oil to progressively increasing temperature, continuously supplying the oil to the pool of lowest temperature and conducting the overflow from each pool to the pool of next higher temperature, in introducing the vapours to a dephlegmator, returning the condensed product to the pool and forcing certain of the remaining vapours from certain stills back through the pool of next lower temperature, collecting the uncondensable gases formed in the process and injecting the same into the pool of highest temperature."

C. P. Dubbs (U.S.P. 1,628,127, May 10, 1927) patents "a process for cracking hydrocarbon oil, which consists in supplying oil under pressure to a heating zone, in passing heated oil from the heating zone to a distilling zone, in taking off vapours from the distilling zone, in controlling the quantity of oil supplied to the heating zone by the liquid level of the oil maintained in the distilling zone, and in continuously maintaining a local cyclic circulation of the oil undergoing treatment in the heating zone."

C. P. Dubbs (U.S.P. 1,628,236, May 10, 1927) presents "a process of converting hydrocarbon oils, which comprises passing a stream of oil through a cracking zone where said oil is subjected to a cracking temperature, in delivering the highly heated oil to an insulated vapour chamber located outside of the cracking zone, and in which chamber a pool of liquid oil collects, in discharging vapours from said chamber to a dephlegmator, in returning reflux condensate from the dephlegmator

to the oil stream passing through the cracking zone, in discharging uncondensed vapours from the dephlegmator to a final condenser and receiver, in removing incondensable gases from said receiver, in heating said gases, and in then passing the heated gases into a conduit immersed in the liquid oil in the vapour chamber, in discharging the gases from said conduit into said oil, and in maintaining a superatmospheric pressure on the oil in the cracking coil and in said vapour chamber."

C. P. DUBBS (U.S.P. 1,638,112, Aug. 9, 1927) discloses a process of cracking "consisting in continuously passing oil through a heating zone where it is subjected to a cracking temperature, in introducing the heated oil to an enlarged vapour chamber, in discharging unvaporized residue from said vapour chamber and preventing it from again coming in contact with the incoming charging stock fed to said heating zone, in taking off vapours from said vapour chamber and passing them through a vapour line to a reflux condenser, in trapping all the condensate produced in said line to prevent any of said condensate from directly returning to the vapour chamber, in returning said condensate, together with condensate produced in the reflux condenser to the heating zone for retreatment, in condensing and collecting the vapours from said reflux condenser, and in maintaining a vapour pressure above atmospheric on the oil undergoing conversion."

C. P. DUBBS (U.S.P. 1,638,113, Aug. 9, 1927) has devised "a process for cracking hydrocarbon oil consisting in converting the oil at a cracking temperature in a partitioned reaction chamber, charging the oil to the portion subjected to the highest temperature, circulating the heated oil to a vaporizing portion, dephlegmating and condensing the generated vapours, collecting the precipitated carbon out of contact with the lower heated portion of said reaction chamber, and drawing off the residual substance with substantial quantities of said precipitated carbon."

C. P. DUBBS (U.S.P. 1,652,166, Dec. 13, 1927) covers "a process for simultaneously dehydrating and cracking petroleum oil, consisting in passing the oil in a confined stream through a dephlegmating zone where said oil is subjected to a temperature above the boiling point of water, and wherein it acts as a dephlegmating medium for the vapours passing through said dephlegmating zone, in then introducing this preheated oil to an enlarged zone wherein the water vapours are relieved from the oil, in discharging such vapours, in continuously taking off dry oil from said enlarged zone and passing it in a restricted stream (pipe coil) through a heating zone, wherein it is raised to a cracking temperature, in thence passing such heated oil to an enlarged reaction zone, in passing the evolved vapours from said zone to said dephlegmating zone, and in discharging the uncondensed vapours from said dephlegmating zone for condensation and collection."

C. P. DUBBS (U.S.P. 1,652,167, Dec. 13, 1927) presents a method for cracking heavy into light hydrocarbons, consisting in passing the oil through a relatively small coil in a heating zone, thence passing the oil through a relatively larger vapour generating coil also seated in said heating zone, taking off vapours from said vapour generating coil, subjecting such vapours to a reflux condensing action, in returning the reflux condensate resulting therefrom to said vapour generating coil, in maintaining a forced cyclic circulation of the oil from said small coil to the vapour generating coil and back to the small coil during the treatment of the oil, and in maintaining a superatmospheric pressure on the oil in said coils."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,618,645, Feb. 22, 1927) describe in an apparatus for cracking "the combination with a still having a stationary portion and a movable portion, means for actuating said movable portion, and a heating element taking the form of a longitudinally disposed tube extending through said portions, an oil feed passing through the stationary portion, and vapour and residuum outlets in said stationary portion."

GUSTAV EGLOFF (U.S.P. 1,619,921, March 8, 1927) devises "a process for cracking oil consisting in passing the oil through a heating zone where it is subjected to the action of heat and pressure, delivering it through a transfer line in substantially liquid form to an expansion chamber where vaporization takes place, taking off the vapours from the end of the expansion chamber remote from its connection with the transfer line, subjecting such vapours to reflux condensation and returning the reflux condensate to said transfer line, where it is mixed with the heated oil and the combined mixture then passed to the expansion chamber." The system may be operated, as illustration, under a pressure of 135 pounds and a temperature of 750° F. (399° C.).

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,619,922, March 8, 1927) describe an apparatus for cracking consisting of a "combination with a shell member comprised of a stationary section and a rotary section forming a still, means for delivering oil to said shell members, of a second shell member comprised of a stationary section and a rotary section forming a vapour chamber, connections between the still and vapour chamber for delivering vapours from one to the other, means for discharging vapours from the rotary section constituting the vapour chamber, and means for rotating said rotary members."

GUSTAV EGLOFF and W. R. HOWARD (U.S.P. 1,627,164, May 3, 1927) include "in an oil distilling apparatus, an elongated horizontally disposed expansion chamber, a conduit for heated oil passing from one end of said chamber substantially through the same and discharging the oil at the opposite end thereof, said chamber having a vertical leg at the discharge end of said conduit, a vapour outlet positioned away from the discharge end of the conduit for discharging vapours from said chamber a dephlegmator communicating with said outlet and a residuum discharge from said leg."

GUSTAV EGLOFF (U.S.P. 1,638,093, Aug. 9, 1927) claims a process of cracking by "passing hydrocarbon oil through a plurality of independent coils, in delivering the oil from each coil to an associated enlarged expansion chamber, in heating the oil while passing through the coils to a cracking temperature, and in maintaining the same both in the coils and in the expansion chambers under a superatmospheric pressure, in discharging vapours from each of said expansion chambers into a single elongated vapour drum, in passing vapours from said drum to a dephlegmator, and in maintaining a superatmospheric pressure in said drum and in the dephlegmator in excess of the pressure maintained in said coils and expansion chambers."

GUSTAV EGLOFF (U.S.P. 1,638,115, Aug. 9, 1927) has developed a process of cracking by passing hydrocarbons "through a heating chamber, under pressure, in discharging the oil in a substantially liquid phase into an enlarged expansion chamber where vaporization takes place, in locally and positively heating the upper portion of said expansion chamber to impart heat to the vapours therein by applying heat to the chamber

substantially along its entire length, in discharging the vapours to a reflux condenser, in retreating the reflux condensate separated from the vapour, and in maintaining the vapour pressure on the oil in said dephlegmator and expansion chamber."

GUSTAV EGLOFF and J. G. ALTHER (U.S.P. 1,638,116, Aug. 9, 1927) secure heat economies in an apparatus for cracking hydrocarbon oils by the combination with a furnace, "of a cracking coil therein, an expansion chamber adjacent said coil into which oil is delivered, a reflux condenser, means for passing generated vapours to said reflux condenser, means for feeding charging stock to the reflux condenser to condense the heavier insufficiently cracked vapours, means for discharging residual oil from said expansion chamber, a pre-heater receiving said oil, means for feeding an independent supply of charging stock to said pre-heater, and means for introducing the heated charging stock from the pre-heater and the reflux condensate and charging stock from the reflux condenser to said cracking coil." Temperature of 850° F. (454° C.) in the coil and 250 pounds pressure are given as illustrative operating conditions.

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,649,102, Nov. 15, 1927) give as their invention "a process of dehydrating and cracking emulsified crude oil consisting in subjecting the oil to surface heating, then applying heat to the lower portion of the oil to further distill and crack it, superheating the generated vapours to further crack them and meantime maintaining a substantial pressure on the oil under treatment, and continuing the process until the oil has been dehydrated and a substantial portion thereof converted to lower boiling point hydrocarbons."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,649,105, Nov. 15, 1927) have devised an apparatus for cracking oil consisting of "a transfer line for a tube and drum oil cracking apparatus adapted to convey heated hydrocarbon oil constituents from the tube into the drum, said transfer line terminating at its discharge end in a plurality of internally rifled nozzles, whereby the hydrocarbon oil constituents passing through said transfer line are subdivided and discharged therefrom at a high velocity in a plurality of circulatory paths." Pressure of 200 lb. and an oil temperature of 895° F. (479° C.) are given as illustrative.

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,655,600, Jan. 10, 1928) claim "in an apparatus for treating oil, the combination with a centrally disposed heating member, of a perforated annular shell rotatably mounted around the heating member and provided with a plurality of agitator blades and a second shell extending around said rotatable shell."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,659,397, Feb. 14, 1928) claim an apparatus for cracking oil, having in "combination with a still having a stationary portion and a rotating portion, means for feeding oil to the stationary portion of the still, a heating element extending through said still, means for rotating the movable portion of said still and said heating element in opposite directions, a vapour discharge from said still, a reflux condenser in communication therewith, means for returning condensate to the still, and means for discharging residuum from the still."

GUSTAV EGLOFF and H. P. BENNER (U.S.P. 1,659,398, Feb. 14, 1928) expose hydrocarbon oil to cracking conditions in a tubular heating zone, deliver the oil into one end of an enlarged reaction zone, and increase the velocity

of the vapours as a function of decreasing the diameter of the reaction zone through which the vapours pass to a dephlegmator. The system is under pressure.

W. F. Faragher and W. A. Gruse (U.S.P. 1,629,908, May 24, 1927) cover "the method of cracking oils in a pressure still, which comprises maintaining a pool of oil and circulating oil from the pool downwardly to one end of heating tubes, thence through the heating tubes, and upwardly back from the other end of the heating tubes to the said pool, heating the oil to a cracking temperature in the said heating tubes, and promoting circulation of the oil through the heating tubes by introducing a current or currents of gas, acting on the "air-lift" principle, into the oil at a point in its passage upwardly between the heating tubes and said pool."

W. F. Faragher and W. A. Gruse (U.S.P. 1,640,444, Aug. 30, 1927) disclose "the method of cracking oils, which comprises subjecting a body of oil in a still to the action of heated surfaces and thereby heating the oil to a cracking temperature under pressure, and introducing a current or currents of gas, acting on the "air-lift" principle, in upwardly directed jets in an upwardly directed passage within the body of oil, the gaseous current or currents being made up of gases produced during the cracking operation."

Richard Fleming (U.S.P. 1,655,053, Jan. 3, 1928) describes "the combination with a pressure oil cracking still, of a pressure vapour line having an adjustable vapour discharge nozzle, and means for interiorly and exteriorly supplying water to condense the vapour discharged from said nozzle by direct contact adjacent the nozzle."

G. E. Fox (U.S.P. 1,659,948, Feb. 21, 1928) claims the "process of transferring hydrocarbon vapours from a heating coil to an enlarged digesting zone in which conversion takes place, comprising passing into a conduit the product from the coil partly in vapour phase and at a pressure not in substantial excess of 50 lb. per square inch (at 680°–700° F. (360°–371° C.)), injecting into the conduit in the direction of travel a stream of gas at a pressure approximating 1000 lb. per square inch (at approximately 900 F. (482 C.)), constricting the flow of the gas for a brief period, and then allowing expansion into the enlarged chamber, whereby the low pressure vapours are forced into such chamber and subjected to a pressure of the order of 350 lb. per square inch therein."

W. S. Hadaway, Junr. (U.S.P. 1,628,143, May 10, 1927) presents "apparatus for cracking hydrocarbon oils, comprising a cracking vessel, a hollow shaft mounted therein and in communication with a source of oil supply for said vessel and rotatable spraying means adapted to receive fluid from said shaft and to be actuated by said fluid."

R. W. Hanna (U.S.P. 1,658,241, Feb. 7, 1928) provides "a process of destructively distilling petroleum oil which comprises distilling an oil under the requisite temperature and pressure to decompose such oil while permitting the products to vaporize, passing the evolved vapours through a three stage separating system under the pressure of the cracking reaction, in the first stage of which system the evolved vapours pass upward against a descending shower composed of the feed oil to the cracking process and the reflux descending from the second stage, in the second stage are scrubbed against the descending shower of condensed vapours from the third stage, and in the third stage are brought to a desired

discharge temperature by dissipation of heat to an independently controlled liquid cooling medium other than the liquid undergoing distillation, and continually passing the combined reflux from the vapour separating system together with said feed oil to the cracking chamber."

E. W. HARTMAN (U.S.P. 1,618,427, Feb. 22, 1927) continuously cracks oil in an apparatus consisting of a combination of a still and a retort against whose heated walls the oil from the still is sprayed. Both still and retort are provided with agitators serving also as scrapers. Unvaporized oil is recycled and the residuum withdrawn.

E. C. HERTHEL (U.S.P. 1,615,583, Jan. 25, 1927) describes "in tubular oil cracking stills a heating flue, a fire-box connected to one end of the heating flue and a stack flue connected to the other end thereof, a battery of oil heating tubes connected in multiple arranged in and extending through the heating flue whereby heating gases passing from the firebox to the stack flue pass thereover in the heating flue, means for circulating oil through the oil heating tubes in a direction generally countercurrent to the flow of heating gases thereover, and means arranged on the oil heating tubes in the said heating flue except those nearest the fire-box for increasing the external surface thereof, the oil heating tubes in the said heating flues nearest the fire-box having the minimum external area exposed to heating gases passing through the heating flue."

E. C. HERTHEL (U.S.P. 1,632,967, June 21, 1927) claims a method of cracking oil under high temperature and pressure "for the production of light hydrocarbon oils containing very light constituents in high concentration, which comprises distilling heavier oil under pressure at a cracking temperature, subjecting the vapours of the cracked oil to a refluxing operation, and introducing fresh oil into the refluxing operation in direct contact with the vapours therein at a rate between about 190 per cent. and 300 per cent. of the rate at which distillate is taken off."

E. C. HERTHEL and H. L. PELZER (U.S.P. 1,634,666, July 5, 1927) cover "the improvement in the cracking of hydrocarbon oils under pressure which comprises heating a charge of the oil in a pressure still to the cracking temperature under pressure, maintaining in said still charge a body of Fuller's earth or similar absorbent material, supported on a support adapted to permit free passage of oil, and extending entirely across the charge of oil in the pressure still, withdrawing oil from beneath said support and circulating it through heating tubes and discharging the oil from said tubes directly into the body of oil above such absorbent material."

R. C. HOLMES (U.S.P. 1,623,729, April 5, 1927) claims "the process of producing low boiling hydrocarbon oils by the conversion of higher boiling hydrocarbon oils, which comprises passing the high boiling oil to be treated once only through a confined passage of substantially uniform cross-section without substantial enlargements, said passage being heated to impart to the oil a temperature of about 700° to 900° F. (371°–482° C.), completing the entire desired conversion in said passage, maintaining upon the oil in the passage a pressure of upwards of 500 lb., the pressure employed being such that the entire oil is maintained in continuous liquid phase during the entire conversion, whereby the entire conversion is effected without substantial production of coke, discharging the completely converted oil into an enlarged chamber to which no additional heat is imparted, said chamber being at substantially reduced pressure whereby vaporization of the desired low

boiling products together with higher boiling products is effected, removing such vapours, separating therefrom by condensation, the products of higher boiling point than the desired low boiling point products, returning separated higher boiling point products to the unvaporized liquid in the chamber, thereby modifying its characteristics and withdrawing completely from the system unvaporized liquid with admixed condensed products from the vapours."

R. C. HOLMES, F. T. MANLEY and O. BEHIMER (U.S.P. 1,646,380, Oct. 18, 1927) carry out the conversion of oil into light hydrocarbons under high temperature and pressure by means of heating the oil in a continuous pipe coil, discharging the same into the bottom of vertical chambers and returning the reflux condensate from the fractionating tower to the vertical tanks. The cracked distillate produced is run to storage.

F. A. HOWARD (U.S.P. 1,649,532, Nov. 15, 1927) claims the process "of pyrogenetically distilling lower boiling point hydrocarbon oils from higher boiling point hydrocarbon oils which consists in passing a stream of oil upwardly through a heated zone to a bulk supply maintained under pressure, and injecting 3 to 7 per cent. of steam upwardly into the oil between the heated zone and the bulk supply."

F. A. HOWARD, E. M. CLARK and J. R. CARRINGER (U.S.P. 1,615,384, Jan. 25, 1927) crack oil at a temperature of the order of 1000° F. (538° C.), and a pressure of 300 lb. for the purpose of producing low boiling oils "having dominant paraffinoid characteristics which consists in continuously flowing the hydrocarbon oil through a zone heated to a temperature sufficient to cause conversion of the oil at a rate of at least 35 per cent. per hour and under a pressure sufficient to maintain the said oil in the liquid phase, and removing the lower boiling point hydrocarbons substantially immediately upon formation during passage through the heating zone."

F. A. HOWARD and N. E. LOOMIS (U.S.P. 1,640,938, Aug. 30, 1927) state that their "method of distilling and converting hydrocarbon oils comprises passing the oil through a heated chamber in which its lighter constituents are removed, passing residues continuously through a heat conversion system wherein it is maintained at a conversion temperature under a pressure sufficient to maintain it substantially entirely in the liquid phase until considerable conversion has taken place, reducing the pressure upon the products of conversion of said residues, separating said products into liquid and vapour constituents, and commingling at least part of the liquid constituents with fresh oil being subjected to fractional distillation."

W. R. HOWARD (U.S.P. 1,627,436, May 3, 1927) treats oil under heat and pressure in a shell still connected with heating tubes below it, and provided with an inner vessel connected to an aerial condenser. The vapours from the large still pass through the reflux condensate which collects in the inner still. The condensate in part undergoes cracking in the inner container, and in part overflows and passes to the heating tubes.

H. A. W. HOWCOTT (U.S.P. 1,641,852, Sept. 6, 1927) claims "in an apparatus for cracking oil, a still composed of a plurality of horizontal pre-heaters, a vertical cracking cylinder interconnected with the said pre-heaters below the oil level therein, stirrers in the pre-heaters, stirrers in the vertical cracking cylinder, means for heating the still, and means for admitting compressed air to the horizontal pre-heaters, and steam to the pre-heaters and still."

L. C. Huff (U.S.P. 1,619,977, March 8, 1927) has devised a process and apparatus for cracking hydrocarbon oils, "consisting in forcing the oil under pressure in a plurality of independent streams through a furnace where said oil is progressively heated, increasing the velocity of the oil approaching the point of highest heat by combining the oil streams into a less number of streams."

L. C. Huff (U.S.P. 1,638,735, Aug. 9, 1927) presents "a process for cracking hydrocarbon oil, consisting in raising the oil to a cracking temperature while flowing in a stream through a heating coil, in delivering the heated oil, subsequent to its passage through the heating coil, to an enlarged reaction zone, in separating removing vapours evolved from the oil and unvaporized liquid oil from said reaction zone, in materially reducing the pressure on the unvaporized liquid oil removed from said reaction zone, to cause substantial quantities of such oil to vaporize by latent heat thereof, isolating the oil unvaporized by said reduction in pressure from the process, in subjecting the vapours released from such unvaporized oil, together with vapours removed from said enlarged reaction zone, while in a commingled state, to reflux condensation, in continuously passing the reflux condensate separated from such commingled vapours undergoing reflux condensation, together with incoming charging oil for the process through said heating coil."

R. E. Humphreys (U.S.P. 1,647,629, Nov. 1, 1927) has devised an "improved method of manufacturing gasoline which consists in distilling a hydrocarbon oil distillate having a boiling point range of 650° to 850° F. (343°–454° C.) under a pressure of 60 to 100 lb. per square inch, separating from the products of such distillation a distillate stock having an initial boiling point approximating the maximum boiling point of gasoline, and redistilling the separated stock under a pressure in excess of 300 lb. per square inch for the further formation of gasoline."

E. W. Isom (U.S.P. 1,650,519, Nov. 22, 1927) covers a process for cracking oil which comprises "heating the oil to a cracking temperature under pressure in a still, passing vapours from the still through a reflux tower, feeding fresh stock into the upper end of the tower in direct contact with the vapours therein, introducing an unheated stream of gas into the lower end of the tower in direct contact with the vapours therein, and conveying admixed fresh stock and reflux condensate from the lower end of the tower to the still."

W. C. Kirkpatrick (U.S.P. 1,646,543, Oct. 25, 1927) covers the cracking of oil to produce low boiling hydrocarbons by means of heating them "to a temperature of about 500° to 600° F. (260°–316° C.) under low pressure (atmospheric), then placing the heated hydrocarbons under a pressure of about 600 to 700 lb. per square inch, delivering the hydrocarbons at that pressure to a still in which the pressure is maintained at about 150 to 200 lb. per square inch and in which a temperature of about 780° F. (416° C.) or more is maintained, atomizing the hydrocarbons at their point of delivery and pressure release into the still, and taking off from the still the resultant carbonaceous deposit and the vapours and gases evolved."

F. A. Kormann (U.S.P. 1,661,804, March 6, 1928) covers "a still for converting high boiling point oil into oil of lower boiling point embodying a still shell, a body of highly absorbent brick held in said shell to leave a vapour dome above and an oil space below the same, means for charging

oil into the shell, and steam admission pipes at the bottom and at an intermediate height in the still shell, whereby steam may be charged into the body of absorbent brick at a plurality of levels."

E. H. Leslie and B. R. Tunison (U.S.P. 1,644,736, Oct. 11, 1927) claim "the process of converting liquid hydrocarbons into products of lower boiling point which comprises bringing together surfaces of liquid bodies of hydrocarbons at a converting temperature at least as high as the boiling point of one of them, one of said bodies of liquid being uniformly distributed over the surface of the other and being intermittently supplied thereto, the temperature of the other body of liquid being higher than that of such distributed body of liquid." The products of such a cracking process are given as the following:—

Gasoline	20 per cent.
Kerosine	15 „
Gas Oil	20 „
Fuel Oil or Residuum	40 „
Loss in cracking and refining	5 „

"However, under very favourable conditions, the gasoline obtained may be as high as 30 per cent."

F. T. Manley (U.S.P. 1,640,202, Aug. 23, 1927) presents "in an apparatus for converting hydrocarbon oils, a furnace of refractory material, a still disposed therein and adapted to be partially filled with liquid oil, means for circulating the heat of combustion around substantially the entire external periphery of said still to apply cracking heat to both the vapour and liquid portions thereof, and a heat insulating medium on the vapour portion of said still above the liquid level to prevent the oil vapour therein from being heated to a temperature materially higher than the liquid oil in the liquid portion and to provide a cracking zone of substantially uniform cracking temperature."

C. Owens (U.S.P. 1,613,124, Jan. 4, 1927) has a cracking process for the production of light oil at a temperature of approximately 750° F. (399° C.).

A. J. Paris, Junr. (U.S.P. 1,614,930, Jan. 18, 1927) describes preliminarily apparatus and a process of cracking close fractions of petroleum "for the production of lower boiling liquid hydrocarbons which comprises preliminarily distilling the petroleum hydrocarbons, compressing and liquefying the distillate continuously passing the liquefied distillate through a converting zone while limiting the boiling range of the fraction subjected to conversion at any given instant to less than about 100° F. (56° C.), and regulating the temperature and pressure in the converting zone to correspond to the character of the distillate as the preliminary distillation proceeds."

C. L. Parmelee (U.S.P. 1,613,718, Jan. 11, 1927) has invented "a process of cracking hydrocarbon oils which comprises circulating oil from a supply chamber through a heating element to a separating chamber, subjecting the oil to a cracking temperature in the heating element, and maintaining the oil in the separating chamber and that in the supply chamber in indirect heat exchanging relation, effecting a separation of carbon and tarry matter in the separating chamber and withdrawing the separated carbon and tarry matter, passing the clarified liquid oil to the supply chamber, collecting the vapours liberated in the separating chamber and the supply chamber and subjecting them

to a refluxing operation, introducing fresh oil into the refluxing operation and passing the admixed reflux and fresh oil from the refluxing operation to the supply chamber."

R. S. PERSHING (U.S.P. 1,661,196, March 6, 1928) projects oil in fine jets upon a cylindrical electric heating element running the length of a horizontal shell still, thereby producing vaporization and cracking.

A. A. PHELAN (U.S.P. 1,646,929, Oct. 25, 1927) passes highly heated oil under pressure into the top of a still, where vaporization takes place while it is passing over a series of inclined plates. The residual oil drops to the bottom of the still and by a baffle arrangement deposits carbonaceous material before reaching the outlet. Temperatures of 700–850° F. (371°–454° C.) or higher and pressure of 50 to 200 lb. may be used.

R. T. POLLOCK (U.S.P. 1,628,270, May 10, 1927) devises "a process of cracking petroleum oil, consisting in subjecting the oil to a cracking temperature under a superatmospheric pressure to cause substantial vaporization, subjecting the generated vapours to a reflux condensing action by passing them, prior to any substantial cooling action, to a reflux condenser, delivering the reflux condensate to a still where it is subjected to distillation at atmospheric pressure to vaporize those constituents that are of the desired pre-determined end point, then returning the unvaporized liquid from the atmospheric still to the cracking zone, and in heating said atmospheric still." During the cracking a pressure of about 150 lb. and temperature of about 700° F. (371° C.) may be used.

H. B. SETZLER (U.S.P. 1,629,810, May 24, 1927) proposes a process "involving the separation of carbon from gas oil to produce gasoline which consists in subjecting the gas-oil to pressure distillation in a volume maintained substantially constant under conditions involving a pressure of from 50 to 100 lb., temperatures of from 700° F. to 750° F. (371°–399° C.), within a highly heated pressure space approximately equal to the volume of gas oil under treatment; meanwhile subjecting the gas oil to suitable means for concurrently scouring the bottom of the still, and advancing the treated hydrocarbons to the point of withdrawal."

G. D. SIMS (U.S.P. 1,658,420, Feb. 7, 1928) arranges "in an apparatus for treating oils, the combination with a reaction chamber adapted to receive oil heated to a conversion temperature and in which chamber said oil is maintained under a superatmospheric pressure, of a vapour outlet from the chamber, a condenser through which the discharged vapours are passed, a receiver in which the cooled condensate and uncondensed gases collect, means for indicating the level of the oil in said chamber comprising a gauge, a liquid oil discharge line from said chamber to said gauge, means interposed in said discharge line for cooling the oil before it is admitted to the gauge, and means for introducing uncondensed gases from said receiver to maintain the oil in the gauge under the pressure maintained on the oil undergoing treatment in the apparatus."

A. D. SMITH and JOHN PERL (U.S.P. 1,640,223, Aug. 23, 1927) have patented "a process of converting heavy hydrocarbon oils into low molecular weight hydrocarbons which consists in cracking the heavy hydrocarbons partly into light gaseous hydrocarbons and partly into semi-liquid polymerized hydrocarbons soluble in the partially converted stock, eliminating said gaseous products and then precipitating and eliminating a portion of such polymerized hydrocarbons, said operations being

effected while the stock is continuously circulated through a zone of heat and pressure sufficient for said cracking operation and thence through a zone of sufficiently low temperature to precipitate such portion of said polymerized hydrocarbons, and thence back to a second zone of heat, fresh stock being added to the treated portion from which said polymerized hydrocarbons have been precipitated after such portion reaches said second zone of heat." The pressure may reach 300 lb. and temperature 850° F. (454° C.) in the first zone, dropping to about 100 lb. and 700° F. (371° C.) in the second zone.

W. O. Snelling (U.S.P. 1,624,848, April 12, 1927) presents "the process of converting petroleum oils which comprises establishing and maintaining a body of petroleum oil and vapours therefrom under such heat and pressure as will produce equilibrium in such body and during the maintenance of such equilibrium slowly withdrawing the liquid products of equilibrium and slowly adding fresh oil." Normally the reaction chamber will show a pressure of about 800 lb., but "by using an equilibrium-promoting catalyst in the oil, such as deflocculated graphite, colloidal nickel, etc., the necessary pressure may be somewhat diminished down to 650 lb. The pressure, with a corresponding temperature, which will be between 400° and 500° C. (752°–932° F.), presuming gas oil to be used, will produce equilibrium in the whole system, an equilibrium between the gases, vapours and high boiling oils."

A. C. Spencer (U.S.P. 1,648,967, Nov. 15, 1927) covers a process which "comprises continuously subjecting a stream of hydrocarbons to a cracking temperature, separating out fractions heavier than kerosine in a series of progressively cooler zones provided with a controlled reflux, then fractionally separating the remaining vapours into kerosine and gasoline by feeding the vapours about midway in a second series of progressively cooled zones provided with a controlled reflux."

F. Tinker (U.S.P. 1,632,011, June 14, 1927) claims a method of treating oil which comprises topping by distillation, partially condensing the vapours, cracking the condensate thus formed, and introducing the cracked vapours into the uncondensed vapours from the topping operation.

M. J. Trumble (U.S.P. 1,659,930, Feb. 21, 1928) operates a shale distilling and cracking process, so that the vapours may do useful work in operating a generator set. The heavier vapour portions from the shale are condensed and used as cracking stock, being subjected to a temperature of about 800° F. (427° C.) while under superatmospheric pressure.

F. C. Vande Water and F. R. Sunderman (U.S.P. 1,655,030, Jan. 3, 1928) patent, in combination, a still body adapted to contain a menstruum oil, a flue for combustion gases passing upwardly through the same, "means for supplying oil in a number of fine streams adjacent the lower portion of said still, a baffle directing the supplied oil upwardly, an inverted bell shape baffle outside and above the first baffle, and means for leading off the vapours formed." The cracking is carried out at atmospheric pressure, the menstruum oil being at about 750° F. (399° C.).

F. E. Wellman (U.S.P. 1,615,799, Jan. 25, 1927) has devised a "method of cracking hydrocarbon oil which consists in dividing the main body of oil under treatment into a plurality of connected bodies, whereby the area available for the external application of heat is proportionately increased, intermittently and individually heating said separated bodies in periodic rotation, whereby a degree of heat greater than could be withstood if continuously applied may be employed without destructive

action, and drawing off the resultant vapours from all the bodies in common while maintaining a common liquid level with extended surface to prevent foaming in the individual bodies."

F. E. WELLMAN (U.S.P. 1,616,521, Feb. 8, 1927) presents "the method of cracking oil which consists in charging a given amount of oil into a still at a given point, heating the oil and taking off the vapours while supplying additional fresh oil at a sufficient rate to maintain substantially the said given amount of oil in the still until said additional fresh oil amounts to substantially the original charge, then supplying fresh oil at twice the rate of evaporation and maintaining substantially the said given amount of oil in the still by drawing off sufficient residuum at another point, and reversing the said points of supply and residuum draw-off during the said heating and taking off of vapours."

F. E. WELLMAN (U.S.P. 1,639,622, Aug. 16, 1927) proposes an apparatus consisting of "a still for the treatment of hydrocarbon oil comprising a plurality of vertical pipes arranged in a circle, concentric annular walls within and without said circle, and means for applying heat intermittently and individually to the still pipes and their contents around the circle in periodic rotation."

G. D. WHITE (U.S.P. 1,621,298, March 15, 1927) devises "apparatus for cracking hydrocarbon oils comprising a battery of spaced vertical stills, a furnace chamber disposed about said stills the walls of which chamber are spaced from the stills, a plurality of gas burners extending through opposite walls of said furnace and spaced from each other horizontally and vertically at points intermediate the several stills, the arrangement being such that heat is applied at a plurality of distributed points within the furnace in such a manner as to avoid direct contact of the flames against the still walls, whereby hot spots are prevented, and a plurality of flue passages spaced from each other in the upper part of the furnace, whereby the furnace gases are caused to travel upwardly through the furnace and are withdrawn at distributed points in the upper part thereof."

L. E. WINKLER and F. C. KOCH (U.S.P. 1,650,813, Nov. 29, 1927) claim an apparatus for treating oil-field emulsions containing relatively large quantities of solids in suspension and cracking the hydrocarbons contained therein, comprising a battery of tanks progressively elevated in series, connections between adjacent tanks for maintaining a predetermined liquid level in each tank by allowing liquid to flow from each tank to the next lower in the series, a spray head in each tank discharging below the liquid level therein, a gas supply pipe for the introduction of highly heated gas communicating with the spray head of the first tank, and connections from each tank above the liquid level therein to the spray head of the next succeeding tank.

E. E. WOLCOTT (U.S.P. 1,654,771, Jan. 3, 1928) covers "the process of converting higher boiling into lower boiling hydrocarbons that comprises introducing a combustible mixture and a quantity of oil into a chamber, firing said mixture under pressure to momentarily subject the oil to a cracking temperature under high pressure and then subjecting the oil to expansion to effect distillation thereof.

English Patents.

C. ARNOLD (STANDARD DEVELOPMENT CO.) (E.P. 274,763, Sept. 14, 1927) passes oil through tubes in a furnace to an enlarged insulated chamber and then at reduced pressure to a second heated chamber, from which

the tar goes to a cooler and the vapours through a bubble tower to a condenser. The oil is pre-heated by passage through the tar cooler and bubble tower.

H. CARROLL (E.P. 284,345, March 21, 1928, not yet accepted) heats liquid hydrocarbons in coils to slightly below cracking temperature, passes the products to a dephlegmator, and cracks the residual liquid by passage in a cascade over troughs containing molten metal.

ROY CROSS (E.P. 273,256, Aug. 17, 1927, not yet accepted) heats oil in tubes in a furnace, passes it to a reaction chamber under high pressure, and then reduces the pressure in passing the oil to a separator and the vapours through a bubble tower to a condenser. Residue from the separator is sent to storage, while that from the bubble tower is pumped into the charging line.

C. P. DUBBS (E.P. 284,507, March 21, 1928) passes oil through a series of heating tubes, and to a reaction chamber at a lower pressure, the vapours then meeting fresh oil in a dephlegmator from which the condensate is returned to the tubes. The uncondensible gas is heated and forced through the oil in the reaction chamber.

C. N. FORREST and H. S. HAYDEN (E.P. 262,959, Feb. 9, 1927) crack bituminous materials, including heavy asphaltic petroleum residues, by mixing them with an inert refractory material and passing the mixture downward through a vertical retort. In the upper portion cracking occurs, while lower down the coke produced burns, furnishing heat for the process.

U. S. JENKINS (E.P. 262,666, Feb. 2, 1927) patents a still in which residuum is continuously removed from a large drum and two transverse drums, and the lighter portions evaporated at reduced pressure. The entering oil is mixed with an absorbent, as Fuller's earth, silica gel, etc.

F. LAMPLOUGH (E.P. 277,419, Nov. 9, 1927) heats finely divided coal mixed with mineral oil under pressure and fractionates the resulting liquid.

C. LONGHI (E.P. 275,281, Sept. 28, 1927) decomposes liquid hydrocarbons by means of an electric arc, which, by reason of the rotation of the electrode, is caused to elongate, is quenched, and a second arc is struck at the same point. Acetylene, carbon black and light hydrocarbons are formed.

W. J. PERELLS (E.P. 271,601, July 20, 1927), in cracking petroleum oils, crude oils or residuals, to obtain gasoline and residual oils suitable as fuel oils, passes the oil in succession through the tubes of three cracking furnaces, the first of which brings it to a cracking temperature, the second allows a small reduction of temperature while maintaining it in the cracking range, and the third again increases its temperature. The treated oil is cooled, before or after releasing the pressure, and is passed into an evaporator. The oil enters the first cracking coil at about 740° F. (393° C.) and leaves the last coil at 860°–910° F. (460°–488° C.) under a pressure of 240–250 lb. or higher.

W. J. PERELLS (E.P. 277,983, Nov. 16, 1927) cracks mineral oils by subjecting a stream of oil while under turbulent flow in a tubular heater under pressure to increase, decrease, and increase of temperature in succession, while the pressure is correspondingly decreasing, increasing and decreasing. The raw material is deprived of its volatile fractions by being forced by a pump through heat interchangers, and then passed

to a container from which it is pumped to the cracking coils. The products from the last coil are passed through a carbon depositing coil into another container, from which the vapours are led through a heat interchanger and a vaporizer into contact with the raw material in a second heat interchanger. The vapour fractions are then led through a pipe to a rectifier. The rectifier separates a vaporous fraction which is passed through a pipe to a heat exchanger and cooler to a storage tank, and a liquid fraction which is collected in a second tank.

T. E. ROBERTSON (E.P. 283,032, Feb. 22, 1928) employs a tube bank through which oils are passed at a cracking temperature. They are then further cracked by use of superheated steam.

SOC. LUXEMBOURGEOISE DES HYDROCARBURES and F. BRIMEYER (E.P. 267,776, May 11, 1927) distil and crack oils in a still, dephlegmate and condense the vapours, re-evaporate them by circulation about the dephlegmator, and pass them through a superheater and hydrogenation chamber. This chamber contains a metallic filling and forms hydrogen from hydrogen sulphide.

S. STRANSKY and F. HANSGIRG (E.P. 267,958, May 11, 1927) effect the heating of pressure cracking stills by means of electrical resistors distributed through the liquid space. An agitator, and means for automatic temperature control may be provided, and the stills may be used in series.

T. TINKER (E.P. 274,959, Sept. 21, 1927) combines a topping and cracking plant, in which pre-heated oil is further heated, the products passed to a vapour separator and the vapours passed through fractional condensers to a final condenser. A part of the condensate from the fractional condensers may be passed through a branch circuit, comprising a still and a vapour superheater. As an alternative, this oil with oil from the vapour separator may be cracked in the branch circuit in the liquid phase, or it may be cracked in part in the liquid phase and then further cracked in the vapour phase.

W. TODT and P. SUMPF (E.P. 267,364, May 4, 1927) obtain saturated motor fuels by cracking mineral oils in successive stages in retorts containing absorptive bodies—*e.g.*, pumice, coke, etc., under proper conditions of time and temperature. The raw materials are vaporized outside the retort, and admitted thereto in fractions of equal boiling point, which are then heated to the temperature and for the time suitable to the particular fraction. The retort comprises a chamotte lined iron tube, packed with absorptive material and heated in a furnace.

Canadian Patents.

G. L. PRITCHARD (Can. P. 267,915, Jan. 25, 1927) claims "the process of cracking petroleum hydrocarbons which comprises maintaining in a still a body of such hydrocarbons under cracking temperature and pressure while withdrawing and condensing vapours of cracked products, agitating the oil and scouring the internal portion of the still where carbon would tend to deposit by a device operated by a shaft passing outside of the still through a packing enclosed in a closed housing, and circulating through the housing a liquid under pressure."

N. E. LOOMIS (Can. P. 267,943, Jan. 25, 1927) covers apparatus comprising a still, a reflux condenser, means for retaining pressure upon the vapours in the still and reflux condenser, a trap out connection in the intermediate portion of said reflux condenser, a cracking coil for receiving such reflux condensate, a vapour separator in connection with said cracking coil, and a condenser in connection with said vapour separator.

German Patents.

A. G. Carburol (D.R.P. 447,755, Oct. 20, 1927) passes high boiling oils through directly or indirectly heated tubes at speeds over one meter per second and temperatures of 400°–450° C. (752°–842° F.), keeping the oil for thirty to eighty seconds at this temperature while in motion and then allowing it to expand.

A. A. F. M. Seigle (D.R.P. 445,657, Sept. 8, 1927) distils and cracks oil by a cyclic process, in which it passes through a retort by a circuitous course about a central heating canal. The oil is thus gradually heated to above its decomposition temperature, and is then passed to a condenser.

U.S. Gasoline Manufacturing Corporation (D.R.P. 440,296, March 17, 1927) heat hydrocarbon oils to a cracking temperature under pressure by causing them to meet a circulating stream of highly heated gas or hydrocarbon vapours.

(*d*) Improvement in Details of Cracking Systems.

U.S. Patents.

J. W. Coast, Junr. (U.S.P. 1,639,327, Aug. 16, 1927) has designed a scraper device for oil stills, especially pressure stills.

A. D. David (U.S.P. 1,655,596, Jan. 10, 1928) employs in a cracking plant reaction chambers used in turn with introduction of cool oil under pressure into a header leading to a chamber that is cut out, so that no hot oils may pass into it during the cleaning operation.

H. J. Halle (U.S.P. 1,619,929, March 8, 1927) covers in an apparatus for cracking petroleum oil, the combination with a coil located in a furnace through which oil is continuously passed, "of a second coil disposed within said coil forming an annular oil passageway, spirally arranged elements mounted between the two coils to space the two coils from each other and act as baffles for the oil passing through said annular passageway, a flue leading from the furnace, means for withdrawing heated gases from the furnace to be passed through said second coil to internally heat the oil passing through said annular passageway."

E. W. Isom and J. E. Bell (U.S.P. 1,623,790, April 5, 1927) patent "the method of cooling and condensing hot hydrocarbon vapours from pressure stills which comprises maintaining a body of condensate thereof, introducing the vapours from said still into said body of condensate near the lower portion thereof with an injector action, whereby the vapours are intimately admixed with the condensate, cooling the body of condensate, and effecting agitation of the body of condensate by the injection of the vapours therein."

E. W. Isom and J. E. Bell (U.S.P. 1,627,544, May 3, 1927) condense vapours from pressure stills in "a plurality of closed condensing tanks arranged in series, each adapted to contain a body of condensate and a body of vapours above the same, cooling means arranged in each of the tanks, means including an expansion nozzle connected with the vapour space of each of the tanks in the series except the last for injecting vapour into the succeeding tank adapted to introduce the vapours into the body of condensate therein, and means for separately drawing off the condensate from each of said tanks."

O. G. Messenger (U.S.P. 1,623,061, April 5, 1927) prepares low boiling chlorhydrocarbons, by vaporizing a gas oil, "passing the vapours at low

pressure through a cracking zone maintained at approximately 750° F. (399° C.) and introducing chlorine into the oil vapours in said cracking zone, the chlorine feed being gauged in view of the products sought."

J. C. MORRELL (U.S.P. 1,618,669, Feb. 22, 1927) claims "subjecting cracked liquid petroleum residue containing suspended pitch-forming, coke-like particles to a segregating action to separate the suspended particles from the liquid medium, in separately withdrawing the freed liquid, and then separately withdrawing the precipitated particles with accompanying oily liquid, and subjecting same to a homogenizing action whereby the suspended particles are substantially stabilized and the mixture assumes a creamy consistency."

A. J. SLOAN (U.S.P. 1,619,440, March 1, 1927) claims "a pressure still for cracking hydrocarbons, having a pressure reducing valve for regulating the escape of vapours from the pressure still to a condenser at a lower pressure, a by-pass around said pressure reducing valve, and an automatic relief valve in said by-pass adapted to open upon a predetermined increase in pressure in the still and to relieve the excess pressure by discharging gases there-through to the condenser."

G. H. TABER, Junr. (U.S.P. 1,663,868, March 27, 1928) adds "in cracking operations for the production of lighter hydrocarbon oils from heavier hydrocarbon oil in which vapours and gases are taken off and subjected to a condensing operation, the improvement which comprises subjecting the gas and vapour mixture remaining uncondensed thereafter first to treatment with an absorbent medium from which absorbed constituents are recovered by treatment independent of the cracking operation, and then subjecting the still remaining uncondensed and unabsorbed gas and vapour mixture to treatment with charging stock subsequently supplied to the cracking operation."

English Patents.

E. P. CRITTENDEN, A. C. KILLINGER and H. L. BOLTON (E.P. 278,944, Dec. 7, 1927) present a device for cleaning reaction chambers of cracking apparatus.

O. KAY (E.P. 276,947, Oct. 26, 1927) cracks hydrocarbon oils by atomizing them in a stream of air and separating the atomized particles according to their gravity. The oil is fed with air to an atomizer, which discharges into a chamber containing a series of vessels arranged transversely into which the atomized particles settle in the order of their densities.

J. F. P. LA RIBOISIERE (E.P. 276,532, Oct. 19, 1927) dephlegmates the vapours from a cracking still by passing them into a constant temperature zone produced by the introduction of a pure liquid or a constant boiling mixture into a tower. The temperature obtained depends on the pressure of the system.

A. E. WHITE (E.P. 273,159, Aug. 17, 1927) provides cracking stills with rotating scrapers to remove carbon from their walls.

(*c*) CRACKING IN BATH OF MOLTEN METAL.

U.S. Patents.

D. E. DELAPE (U.S.P. 1,652,563, Dec. 13, 1927) cracks and distils hydrocarbons in an apparatus including a chamber having a circuitous passage, separate and independently operating heating means for different courses of said passage, a body of molten material in the passage, pieces of material in the molten body of a higher melting point than said

molten body, means to prevent some of the pieces of material from floating to the surface of the molten body and means for introducing material to be treated into the lower course of the circuitous passage.

W. C. Wells and F. E. Wells (U.S.P. 1,635,519, July 12, 1927) claims "the process of breaking up hydrocarbons into more volatile products by submerging them for decomposition in a heated molten metal bath which consists in protecting incoming streams of hydrocarbon against decomposing temperature in the ducts through which they are introduced into said bath, subjecting the said hydrocarbon to the heat of said bath, subjecting all of the vapours thus produced to uniform degree of heat in their passage through said bath to the surface thereof, and expelling all hydrocarbon into said ducts of compressed gas."

English Patents.

C. F. Hammond and W. Shackleton (E.P. 265,253, March 30, 1927) propose to crack oil in an apparatus in which a heated molten bath is used, outside of which the oil circulates.

H. J. Jansen (E.P. 278,235, Nov. 23, 1927) passes oils horizontally through molten material, preferably molten lead with a layer of zinc chloride above it. High carbon oils are subjected to preliminary cracking in a special apparatus.

C. D. Maxe (E.P. 263,381, Feb. 16, 1927) desulphurizes and hydrogenates heavy liquid hydrocarbons by passing them with steam into a heated chamber in contact with catalytic metals, which may be in the molten state.

S. Seelig (E.P. 268,323, March 11, 1927, D.R.P. 443,463, June 23, 1927) passes oils into the bottom of a heated vessel containing molten metal. To prevent fluctuations in temperature, a helix is placed between the walls of the vessel and the central reaction zone, and through it gases may be passed.

S. Seelig (E.P. 269,490, June 9, 1927, not yet accepted, D.R.P. 444,986, Aug. 11, 1927) adds to E.P. 268,323 the use of the oil to be cracked as the medium circulating through the temperature equalizing worm.

German Patents.

Erwin Blümner (D.R.P. 437,613, Jan. 20, 1927) lessens coke formation in the cracking of mineral oils and tars by the addition of high boiling, stable oils from coal tar, such as anthracene oil.

Erwin Blümner (D.R.P. 439,712, March 10, 1927) secures continuous distillation and cracking of mineral oils by mixing them with gases, such as hydrogen, and passing the mixture in finely divided form through a bath of molten metal containing catalysts.

(*f*) Automatic Control of Cracking Equipment.

Poole[55] points out the advantages of automatic control of oil distillation, particularly in pressure stills, and outlines a modern system of regulation.

De Florez[56] takes up refinery control, and with reference to cracking distinguishes between taking readings of factors which

[55] *Oil and Gas J.*, Oct. 13, 1927, p. 34.
[56] *Oil and Gas J.*, March 1, 1928, p. 106.

merely show that the equipment is capable of functioning, such as steam pressure and fuel supply, and factors such as temperature and pressure which must be more closely watched because they directly affect the quality of the products.

C. B. Faught and F. R. Staley[57] also discuss automatic control of refinery operations, particularly of cracking.

U.S. Patents.

L. C. Huff (U.S.P. 1,652,171, Dec. 13, 1927) has devised an automatic control for pressure systems comprising means for maintaining a predetermined vapour pressure in an oil collecting chamber, a liquid drawoff from this collecting chamber, with a liquid metering gauge in the drawoff, and beyond it a float valve functioning to maintain a predetermined liquid level in the collecting chamber, and to release the pressure on the liquid subsequent to its passage through the metering gauge.

F. M. Poole (U.S.P. 1,615,482, Jan. 25, 1927) introduces into "a tubular oil heater comprising tubes connected to form an elongated path of flow for the oil to be heated, means regulating the supply of heat to said tubes, comprising control means jointly responsive to the temperature of the oil at a plurality of points along said path of flow between which a difference in oil temperature exists, and at each of which the oil temperature is different from the oil temperature of either end of said path."

(*g*) Tempering of Furnace Gases.

Recirculation of a portion of the gases leaving a cracking still furnace as a means of reducing the temperature of the furnace gases before they strike the tubes, and for heat economy, has come into operating practice. Mekler[58] considers the recirculating furnace the most suitable apparatus for heating by convection where low furnace temperatures must be maintained. He states that recirculation not only provides a method of lowering the temperatures of the products of combustion, but by returning to the furnace the heat content of the gases at their final temperature, it recovers a large portion of heat which otherwise would be lost.

He finds that the convection type oil still designed either for topping or cracking is particularly suitable for the application of flue gas recirculation. The fuel saving depends upon the degree of air preheat used, the maximum gas temperature, the flue gas temperature and the recirculation ratio. It may reach 60 per cent. He illustrates and discusses various furnace designs. He concludes that the recirculation furnace, while not yet at its fullest development, will produce a milder heat application, give larger throughput

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[57] *Ref. Nat. Gas. Manfr.*, May, 1928, p. 69.

[58] *Oil and Gas J.*, March 1, 1928, p. 208. *Ref. Nat. Gas. Manfr.*, March, 1928, p. 82.

with the same amount of heating surface, and perform the heating with less fuel and better efficiency than the non-recirculating convection furnace and in many cases than the radiant heat furnace.

U.S. Patents.

J. E. Bell (U.S.P. 1,617,297, Feb. 8, 1927) claims "an oil cracking still having a heating chamber with oil-heating surfaces therein, a firebox communicating with said chamber, means for pre-heating air with the hot gases leaving the heating chamber, and means for tempering the hot products of combustion from the firebox with the pre-heated air before the admixed air and combustion gases enter the heating chamber.

J. E. Bell (U.S.P. 1,623,773, April 5, 1927) covers "the improvement in the heating of oil cracking stills in which oil is heated to the cracking temperature by hot products of combustion from a firebox passing externally over the oil-heating surfaces of the still, which comprises admixing a portion of the hot waste heating gases which have previously passed over the heating surfaces with the products of combustion from the firebox before passing them over the heating surfaces of the still, pre-heating air by heat interchange with waste heating gases not to be returned as a diluent, and supplying the air so pre-heated to the firebox for combustion of fuel therein."

J. E. Bell and E. W. Isom (U.S.P. 1,641,941, Sept. 6, 1927) place in an oil cracking still "a drum, partitions in the drum dividing the same into communicating compartments, means for feeding the oil into the compartment at one end of said drum, a furnace having a series of heating flues communicating with a firebox, heating units connected to the respective compartments and progressively arranged in the flues, the heating unit connected to the supply compartment being nearest the firebox, and means for returning a portion of the products of combustion from a point in the heating flues more remote from the firebox in the furnace to a point less remote therefrom." Pressure of 90 to 300 lb. are given as illustrative.

J. W. Bell and E. W. Isom (U.S.P. 1,660,856, Feb. 28, 1928) devise "an improved method of cracking hydrocarbon oils, which comprises heating the oil to a cracking temperature under pressure in two stages, circulating oil from the first stage to the second stage, supplying fresh oil to the first state, subjecting the vapours from the cracking operation to a refluxing operation and returning reflux therefrom to the first stage, circulating heating gases for supplying the heat absorbed by the cracking operation in indirect contact heat exchanging relation first with the oil in the first stage, and then with the oil in the second stage, and re-circulating part of the heating gases from the second stage and admixing them with the heating gases in the first state."

E. C. Herthel (U.S.P. 1,660,647, Feb. 28, 1928) discloses "an improved method of operating externally heated pressure stills for cracking hydrocarbon oils, which comprises passing heating gases for supplying heat to the cracking operation first over an auxiliary heating coil and then over the heating surfaces of the pressure still proper, admixing hot gases at a lower temperature than the said heating gases with the said heating gases at a point in their passage between the auxiliary heating coil and the heating surfaces of the still proper, and circulating substantially tar free oil through the said auxiliary heating coil to the pressure still proper."

E. W. Isom (U.S.P. 1,661,073, Feb. 28, 1928), in the operation of externally heated single pass tubular oil cracking stills, devises an improvement comprising forcing a stream of oil once through heating tubes and "circulating the hot products of combustion over the oil-heating tubes in a direction generally counter-current to the flow of oil therethrough, whereby the temperature of the heating gases last contacting with the heating conduit is reduced to below the temperature at which the hot oil products are discharged from said heating conduit, re-circulating part of the said heating gases which have passed over the oil-heating tubes and admixing them with the fresh hot products of combustion and circulating the resulting mixture of heating gases over the oil-heating tubes."

John Primrose (U.S.P. 1,654,347, Dec. 27, 1927) presents in an oil still in combination "a fire chamber having a checkered bottom, a combustion zone disposed at a point, spaced from and above said bottom, means for forcing air through said bottom to reduce the temperature of the hot gases of the combustion after combustion has taken place, said bottom serving to uniformly distribute said air in said products of combustion, a bridge wall, and a bank of oil pipes placed back of the bridge wall, over which pipes the hot gases of combustion and the introduced and uniformly mixed air flow downward and counter to the current of oil passing through the pipes, said bridge wall and supplementary air co-operating to prevent over-heating of the oil passing through said pipe."

(4) Vapour Phase Cracking.

Gasoline produced in the vapour phase is relatively high in anti-knock properties. Some of the proponents of vapour phase processes claim it to be equal to benzene for blending purposes. It is natural, therefore, that the expanding market for non-detonating fuel should cause refiners to take new interest in vapour phase cracking.

De Florez[59] has published an analysis of the important factors in vapour phase cracking. He considers a temperature of 1000° F. (538° C.) as about the demarcation line between the liquid-vapour and strictly vapour phase cracking, in which latter the temperature may be carried to 1400° F. (760° C.). At such temperatures pressure is not needed to accelerate the reaction, but it may aid in lessening the production of incondensible products. Vapour cracking produces an antiknock fuel and a large amount of gas. The heat transfer problem can best be solved by passing the gases through small tubes at high velocity in turbulent flow, obtaining about 30 per cent. gasoline in one pass. Cores in the tubes produce uncertainty of flow, and are undesirable. The tubes should be replaceable as no metal will fail to be affected to some degree by oxidation at above 1000° F. (538° C.). Refining losses are greater

[59] *Amer. Petr. Inst.*, 1928, **9**, 159. *Nat. Petr. News*, Dec. 7, 1927, p. 32. *Oil and Gas J.*, Dec. 29, 1927, p. 277.

than with the liquid phase product. In this type of operation high yields of motor fuel are obtained from light distillates, and from stocks too light for liquid phase cracking. Fuel consumption without heat interchange should be around 10 per cent. Steam is sometimes used to prevent overheating, but it should not be necessary and its use may give emulsions. Catalysts are believed to be ineffective.

Francis[60] states that vapour phase cracking has the disadvantages of large gas loss, colour and high unsaturation of the gasoline and poor heat transfer during the process so that overheating is likely to occur.

A vapour phase process called the "Gyro" is described by Truesdell,[61] who states that atmospheric pressure is used and that any oil which can be vaporised may be cracked. The oil is heated in a tube still and the unvaporised portions removed in an evaporator as fuel oil. Three per cent. of steam is added to the vapours, and provision made for removal of entrained oil. The vapours pass through a converter at 1100° F. (593° C.) and over a ferric oxide catalyst. They then heat exchange with the incoming oil and pass to a fractionating tower and to a second tower where they are freed of polymers and high boiling oils with fuller's earth. Yields of gasoline are stated to be 60 per cent., with 15 per cent. fuel oil and 25 per cent. gas. The composition of Gyro gasoline is reported as:

Naphthene hydrocarbons	..	..	15·1 per cent.
Olefine "	..	..	50·1 "
Aromatic "	..	..	34·9 "
Paraffin "	..	..	0 "

Leamon,[62] in outlining his process, states that fresh oil and reflux pass through heat interchangers to heating coils. At a predetermined temperature the oil and vapours pass to a tar drum where tar and heavy oils are collected. The vapours are then raised to as high a temperature as possible without carbonisation, passed into a catalytic zone, to heat interchangers and then to a fractionating column and condenser. The gasoline is stated to contain no paraffins and to be equivalent to a 30 to 40 per cent. benzol blend.

Little[63] reports that he has a vapour phase cracking process in operation on a small commercial scale, with a forty-five day cycle

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[60] *Oil and Gas J.*, Oct. 20, 1927, p. 176; Dec. 29, 1927, p. 248. See also *Petr. Times*, 1928, **19**, 378.

[61] *Nat. Petr. News*, Nov. 16, 1927, p. 20 *Cf.* also Osterstrom, *Oil and Gas J.*, Mar. 1, 1928, p. 226.

[62] *J. Soc. Automotive Eng.*, 1927, **20**, 67.

[63] *Petr. Times*, 1928, **19**, 378.

and no carbon deposition. No details have been published. This plant is now shut down.

Sachs[44] describes the Knox process as operated by the Petroleum Conversion Corporation at Texas City, Tex. The oil is vaporised by a circulating gas stream, and the vapours heated to cracking temperature by mixing with heated gases. Pressure of about three atmospheres and a temperature between 535°—570° C. (995-1058°F.) are stated to be the most favourable for the production of anti-knock gasoline.

Vapour Phase Cracking.

U.S. Patents.

R. K. Collins (U.S.P. 1,654,580, Jan. 3, 1928) covers a process of cracking hydrocarbons "which consists in feeding the hydrocarbon in its vapour phase vertically through a space pierced by a plurality of heat radiating zones which heat the vapour to substantially the same intensity so that each thermo-chemically effective vapour conversion zone substantially abuts in unobstructed and non-overlapping relation with the outer portions of the like adjacent heating zones."

C. S. Corning (U.S.P. 1,652,394, Dec. 13, 1927) discloses the method of cracking "hydro-carbon oils consisting in flowing a higher boiling liquid hydro-carbon mixture containing low boiling hydrocarbons over a series of heated surfaces so as to produce vapours of low boiling point and separately withdrawing different fractions of vapours of low boiling point from the residue at a succession of points, thence cracking the vapours separately by heating same in the cracking zones and thence withdrawing the cracked vapours from the cracking zones and immediately blending them." An apparatus is described.

W. L. Coultas, Junr. (U.S.P. 1,628,532, May 10, 1927) covers "the process of treating hydrocarbon oils which consists of passing the oil through a furnace having a series of coils of gradually increasing temperature which will raise gradually the temperature of the oil until it has reached the vapour point at approximately 500° F. (260° C.), introducing into the oil vapour free hydrogen at a temperature of approximately 1400° F. (760° C.) to form the vapour of another hydrocarbon, passing the new formed hydrocarbon vapours to a distilling column, condensing the vapours of high boiling point, fractionating out the vapours of low boiling point by the heat of the condensate, and passing the condensate from the vapours of high boiling point to a second furnace for repeating the above steps." The vapours may be filtered with fuller's earth as part of the process.

V. W. Northrup (U.S.P. 1,642,624, Sept. 13, 1927) presents "the method of converting heavier hydrocarbons into lighter hydrocarbons, which comprises producing a mixture of vapours of said heavier hydrocarbons and a gas having available hydrogen, subjecting the same to an alternating current field of 2000 to 8000 volts in one zone, whereby the reaction mass is electrified without substantial cracking taking place, and then catalyzing (with Al. Ni. Co. Pd. or Fe.) at temperatures of about 725° F. (385° C.) to 1000° F. (538° C.) in another zone which is independent of said first-mentioned zone."

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[44] *Rev. Petrolifere*, Nov. 26, 1927, p. 19.

H. O. Swoboda and E. M. Richards (U.S.P. 1,616,515, Feb. 8, 1927) include "in a cracking apparatus, a concentric system of conduits, means to supply oil to the inner of said conduits, means to supply a pre-heating agent to the outer of said conduits, means to deliver a current of steam under pressure into said inner conduit, means to supply heated oil to the current of steam, automatic means to maintain the pre-heating agent at pre-determined temperatures at different sections of the concentric conduits, a catalyzer, controllable means to independently heat said catalyzer, and a valved discharge outlet to deliver a controlled portion of the cracked oil from said catalyzer." The catalyzer may be molybdenum, vanadium, etc., and is usually maintained at 1000° to 1100° F. (538° C. to 593° C.).

S. L. Tingley (U.S.P. 1,627,937, May 10, 1927) devises "a cracking and distillation apparatus comprising a furnace, a coil within said furnace for heating the hydrocarbon oil and means for supplying oil to the same, a jacket entirely surrounding said coil and means for supplying water thereto and causing it to flow in the same direction as the flow of the oil whereby it will be converted into superheated steam by the heat of the furnace, and the oil progressively heated, vaporized, and the vapours superheated at substantially the same progressively increasing temperatures as those of the water and its vapour, the oil containing coil protected from direct exposure to the heat of the furnace."

S. L. Tingley (U.S.P. 1,627,938, May 10, 1927) presents "an oil cracking and distillation apparatus comprising means for vaporizing the oil and highly heating the vapour thereof, means for producing and superheating steam to substantially the same temperature as that of the oil vapour, means for subjecting a portion of the superheated steam to the influence of a substance capable of catalytic-like action (as nickel gauze) upon said superheated steam to facilitate dissociation thereof, means for subjecting the highly heated hydrocarbon vapours to the emanations of a radioactive substance, and also to the activating influence of the ultra-violet ray and means for mixing the activated hydrocarbon vapours with the superheated steam and its dissociated elements."

C. P. Tolman (U.S.P. 1,643,036, Sept. 20, 1927) claims in a "method of cracking hydrocarbon compounds the steps which consist in vaporizing mercury, superheating the produced vapour to above the desired cracking temperature, subjecting the hydrocarbon to vaporizing conditions, but without causing substantial cracking thereof and commingling the hydrocarbon vapour produced with said superheated mercury vapour, said mercury vapour being of such thermal quality as to temperature and heat units as to constitute substantially the sole source of heat for said cracking reaction."

W. E. Trent (U.S.P. 1,619,896, March 8, 1927) patents "a process of oil conversion, consisting in passing charging stock through a heat interchanger where a portion thereof is vaporized in subjecting said heated vapours to a compression sufficient to raise the same to a cracking temperature, and in passing said vapours to said heat interchanger to supply heat to vaporize the charging stock." Subjecting vapours at 500°–600° F. (260°–316° C.) to 100 lb. pressure, thus raising them to 700°–950° F. (371°–510° C.) are illustrative conditions.

C. W. Turner (U.S.P. 1,647,026, Oct. 25, 1927) vaporizes oil in the presence of steam, superheats the mixture under pressure in a series of containers, and brings about fractional condensation in an extended series of separators.

W. S. YARD and E. N. PERCY (U.S.P. 1,643,401, Sept. 27, 1927) present a method of cracking heavy hydrocarbon liquids, "which consists in spraying heavy hydrocarbon liquids upon a deep bed of solid fuel in condition of incandescence and contained within a closed chamber, whereby the liquid will come into intimate contact with the fuel and will be vaporized, thereafter passing the vapours into a second chamber over a mass of finely divided carbonaceous material electrically heated to incandescence, subjecting the vapours and the carbonaceous material to the action of steam to prevent plugging of the carbonaceous material with the products of cracking, and then passing the vapours through the carbonaceous material to bring them into intimate contact with the particles of heated carbon and thus bring about a cracking action of the vapours."

English Patents.

E. S. ANDREWS (E.P. 285,199, April 4, 1928) partially vaporizes oil in a tube bank, passes the heavier ends into a second coil where steam is being generated, and the oil vapour and steam through other tubes connected with a series of fractionating condensers. The tubes may be formed of an alloy containing silicon, iron or calcium to act catalytically.

R. K. COLLINS (E.P. 280,034, Dec. 30, 1927) cracks oil vapours in a cylindrical chamber transversed by electrical heating elements or pipes carrying furnace gases.

R. K. COLLINS (E.P. 280,039. Dec. 30, 1927) adds to the process of E.P. 280,034 the passage of steam or permanent gas with the vapours to be cracked.

I. G. FARBENINDUSTRIE (E.P. 268,774, June 1, 1927) (not yet accepted) forms low boiling oils by passing tars and mineral oils, after purification in the vapour phase, together with water vapour or hydrogen containing gases over catalysts at a temperature higher than that required for hydrogenation (250°–700° C.) (482°–1292° F.). Metallic catalysts or oxides activated by a variety of oxides or salts are named. The operation is carried out at atmospheric or reduced pressure.

P. GRÈNE (E.P. 285,668, April 18, 1928) converts oil or tar into light and stable hydrocarbons by passing it in the vapour phase, together with suitable neutral gases, through tubes, each of which is packed, in succession, with (*a*) a non-metallic catalyst; (*b*) an oxide of manganese; (*c*) a second layer of the non-metallic catalyst; (*d*) a hydrogenating catalyst, such as nickel.

H. MARCHAND (E.P. 275,642, Sept. 28, 1927) (not yet accepted) retorts heavy hydrocarbons mixed with powdered carbonaceous material, and cracks and hydrogenates the vapours.

V. W. NORTHRUP (E.P. 275,120, Sept. 21, 1927) causes hydrocarbon vapours mixed with gas having available hydrogen to pass through an electrified zone and thence to a catalytic chamber containing metals.

PETROLEUM CHEMICAL CORP. and E. P. STEVENSON (E.P. 273,781, Aug. 31, 1927) crack gas oil and other petroleum products to obtain a gas for carburetting water gas, etc., intermediate products such as a motor spirit fraction and olefines. The oils are vaporized in a still, and the vapours, which may be superheated, are passed through cracking tubes that pass through a retort heated to between 550°–650° C. (1022°–1202° F.). The cracked products pass through a chamber divided by a baffle to separate tar, and upwards through a dephlegmator down which the oil to be cracked may be passed.

Soc. Internationale des Procedes Prudhomme Houdry (E.P. 267,512, May 4, 1927) (not yet accepted) distil oil or other carbonaceous material, and pass the vapours through a dephlegmator, desulphurizing plant, and catalytic chambers where hydrogenation, polymerization and breaking down occur.

German Patents.

Werschen-Weissenfelder Lignite A.-G. and Arthur Fürth (D.R.P. 439,010, Feb. 24, 1927) pressure distil oils and bring the vapours in contact with a catalyst arranged in a ring shape so that returning reflux condensate does not come in contact with it.

Werschen-Weissenfelder Lignite A.-G. and Arthur Fürth (D.R.P. 439,520, March 3, 1927) crack in the vapour phase using a catalyst heated electrically.

5. Cracking with Catalysts.

(a) Aluminium Chloride.

U.S. Patents.

C. B. Buerger (U.S.P. 1,623,025, March 29, 1927) presents a conversion process which comprises distilling high boiling hydrocarbons "in the presence of aluminium chloride and passing the vapours, together with any hydrochloric acid produced, to a scrubbing device holding a column of water, contacting the vapours in the scrubbing device with sufficient water added above the column to condense hydrocarbon vapours, and to dissolve any hydrochloric acid while cleaning such vapours of chlorides and other impurities, delivering the water, the hydrochloric acid solution and condensed vapours as well as separated impurities, below the level of the column of water and allowing gravitational separation of the condensed hydrocarbons and the water, withdrawing the condensed hydrocarbons, maintaining the column of water substantially constant by continuous withdrawal of a portion thereof, and removing from the column of water all solid collected sludges, such as products formed from the chlorides in the vapours."

J. C. Clancy (U.S.P. 1,620,075, March 8, 1927) claims in a continuous "process of converting higher boiling oils into lower boiling oils, the combination of steps which comprise introducing a stream of a mixture of such higher boiling oils and aluminium chloride into the upper end of a sealed retort having a portion thereof maintained at a temperature to effect an oil cracking reaction therein, delivering into contact with the said oil mixture a stream of a metal chloride which is capable of holding in suspension a portion at least of the carbon separated out in said reaction, the said metal chloride (usually zinc chloride with sodium chloride) being in molten condition, preventing the accumulation of carbon deposits in the retort by allowing said molten chloride containing such suspended carbon and the unvaporized oil, carrying its quota of separated carbon in suspension, to discharge from the retort, and collecting the evolved vapours of lower boiling oils and aluminium chloride from the retort."

P. Danckwardt (U.S.P. 1,665,406, April 10, 1928) claims "the process of distilling oil with aluminium chloride and continuously regenerating the spent aluminium chloride, which consists in withdrawing during the distillation the aluminium chloride hydrocarbon formed continuously from the still, to prevent the formation of gritty carbon, disintegrating

it mechanically by a blast of gases, simultaneously causing a separation of the part transformed into the finest mist from the less disintegrated part, which is allowed to run back to the supply tank for retreatment, forcing the finer part together with the gases through molten metal, and returning the volatilized aluminium chloride and hydrocarbon to the still."

F. W. HALL (U.S.P. 1,647,445, Nov. 1, 1927) prepares a reactive compound adapted for treating hydrocarbon oils by a process which comprises absorbing aluminium chloride vapours in liquid hydrocarbon oil, and treats oil with aluminium chloride by bringing "a descending current of liquid oil into contact with an ascending current of aluminium chloride vapours."

F. M. HESS (U.S.P. 1,625,467, April 19, 1927) claims "in a cracking system of hydrocarbon distillation, the combination of a still, a primary dephlegmator, a vapour conduit leading from said still to said primary dephlegmator, a secondary dephlegmator, a vapour conduit leading from said primary dephlegmator to said secondary dephlegmator, means for introducing a catalyzing agent (aluminium chloride or other substance) into the presence of the vapour in said secondary dephlegmator and an automatic pressure controlling device interposed in said last-named vapour conduit."

A. M. MCAFEE (U.S.P. 1,636,144, July 19, 1927) provides "in the production of oils of lower boiling point by distillation of oils with aluminium chloride, the process which comprises distilling a body of oil for a time with aluminium chloride which is exhausted or partially exhausted from prior treatment of oil, condensing and collecting evolved aluminium chloride vapours together with the oil so distilled, and once more distilling the oil with aluminium chloride, the chloride used in the second distillation including that evolved and collected from the first distillation together with additional aluminium chloride, and the chloride used in the first distillation including exhausted or partially exhausted sludge from the subsequent distillation."

R. DE M. TAVEAU (U.S.P. 1,645,553, Oct. 18, 1927) describes "the process of converting higher boiling hydrocarbons into lower boiling ones that comprises maintaining a body of oil in a still, applying heat to the bottom of the still to heat the oil to a vaporizing temperature while retaining a quiescent pool of aluminium chloride material within said still, said pool being spaced and separated from the heated bottom of the still, periodically charging fresh oil into the still and adding aluminium chloride to said pool and separately drawing off liquid from said pool and from the bottom of the still."

English Patents.

ALLGEMEINE GES. FÜR CHEMISCHE INDUSTRIE (E.P. 271,042, July 6, 1927) convert high boiling hydrocarbons, freed from substances soluble in liquid sulphur dioxide, into low boiling oil by treating with aluminium chloride or its double compound in two steps. The more easily decomposed hydrocarbons are split by the action of about 2 per cent. of the halide, and the residue, if not used as white oil or Diesel oil, treated with an additional 6 per cent. of this reagent.

ALLGEMEINE GES. FÜR CHEMISCHE INDUSTRIE (E.P. 272,433, Aug. 4, 1927) split heavy hydrocarbons with aluminium chloride or a double compound

thereof, by adding a few per cent. at a time and repeating the treatment several times. Before each cracking the oil is freed from unsaturated compounds by extraction with liquid sulphur dioxide. *Cf.* E.P. 271,042.

ALLGEMEINE GES. FÜR CHEMISCHE INDUSTRIE (E.P. 273,999, Aug. 31, 1927) improve the aluminium chloride process of E.P. 272,433 by extracting the residue after the first distillation with the halide with sulphuric acid in place of liquid sulphur dioxide.

A. J. H. HADDAN (E.P. 267,386, May 4, 1927) forms low boiling products by heating high boiling oils to moderate temperatures with 1 to 3 per cent. of aluminium chloride and removing the vapours without refluxing.

Canadian Patent.

A. MCAFEE (Can. P. 270,738, May 17, 1927) distils high boiling petroleum hydrocarbons with not over 3 per cent. of aluminium chloride, removing the vapours as produced until at least 75 per cent. of the charge is collected as distillate, which contains at least as much kerosine fraction as gasoline.

Delbridge[65] makes the statement: "The use of aluminum chloride for cracking now appears to be commercially successful and important."

(*b*) OTHER CATALYSTS, INCLUDING HYDROGENATION PROCESSES.

Krauch[66] discusses high pressure hydrogenation largely as applied to coal, but speaks of its applicability to heavy petroleum oils, in combination with usual cracking processes.

U.S. Patents.

J. C. CLANCY (U.S.P. 1,651,114, Nov. 29, 1927) claims a "method of cracking hydrocarbon oils and manufacturing cyanides which comprises distilling such oils in contact with a molten alkali metal cyanide reagent under superatmospheric pressure, collecting the evolved hydrocarbon vapours and gases, reconstituting the cyanide decomposed in the distilling step and liberating the cyanide trapped in the distillation residues, by subjecting the latter to a cyanide-forming reaction in which participate alkali and nitrogen to combine with a part at least of the carbon content of said residues to form additional alkali metal cyanide, thereby reclaiming the cyanide reagent in admixture with the additional cyanide produced through the intermediacy of said cyanide forming reaction." Pressure of 100 lb. and temperatures of 550°–600° C. (1022°–1112° F.) are given as illustrative.

J. C. CLANCY (U.S.P. 1,658,116, Feb. 7, 1928) covers "the process of producing gasoline like material from heavier oil which comprises flowing said oil in the presence of hydrogen into contact with a molten body containing sodium cyanide through a retort filling of nickel packing units maintained at cracking temperature, supplying the said molten body to and withdrawing the reaction products comprising molten material and unvaporized oil from the retort filling of packing units through liquid sealed passages, and collecting the evolved vapours and gases from the retort."

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[65] *Oil and Gas J.*, Sept. 22, 1927, 58.
[66] *Petr.*, 1927, **23**, 1213, 1240.

G. O. Curme, Junr. (U.S.P. 1,646,349, Oct. 18, 1927, *cf.* also Can. P. 268,569, Feb. 22, 1927) patents "the process which comprises thermally decomposing hydrocarbons (at temperatures as high as 1,000° F. (538° C.)) while the latter are in contact with an alloy consisting predominantly of chromium and iron."

H. T. Darlington and R. M. Steffen (U.S.P. 1,614,660, Jan. 18, 1927) covers "the process of treating hydrocarbons under conditions of temperature and pressure conducive to cracking, which includes the dispersion throughout the hydrocarbon of a previously prepared gel composed of a natural colloidal cracking agent having catalytic properties (such as bentonite-like material) and water.

F. M. Hess (U.S.P. 1,638,335, Aug. 9, 1927) covers "a process of cracking oil, which consists in distilling the oil under pressure in a still, simultaneously generating from a part of the residual products of distillation by internal combustion thereof in a separate chamber and within restricted temperature limits under the pressure existing in the still and in the presence of hot air and steam, a hot gas rich in hydrogen, transferring a part of the heat of said gas to the oil in process of distillation and to the said air and steam out of contact with said oil, air and steam, introducing said gas into the presence of the vapours of distillation while the latter are under pressure, and transferring heat from the remaining part of the residual products of distillation to the oil in process of distillation and to the said air and steam."

E. T. Hessle and W. Lelgemann (U.S.P. 1,658,985, Feb. 14, 1928) claim "an apparatus for the conversion of heavy hydrocarbon oils into lighter hydrocarbon oils, a closed receptacle and atomizing device mounted thereon having a discharge end projecting into said receptacle, said atomizing device having oil and gas conduits therein for separately conducting oil and gas to said discharge end, opposed oil and gas nozzles mounted on said discharge end adapted to cause an impact between the discharging streams of oil and gas, and a needle valve passing through said oil conduit adapted to control the flow of oil therethrough having a projection thereon adapted to pass through said oil and gas nozzles to clear them of obstructions."

H. M. Lasher (U.S.P. 1,622,452, March 29, 1927) claims the combination of a still for cracking hydrocarbons and a rack to hold catalytic material (such as carboniferous matter), with means for suspending said rack within the still and means for adjusting the vertical position of said rack from without the still.

H. M. Lasher (U.S.P. 1,622,453, March 29, 1927) proposes "the method of cracking hydrocarbon oil which consists in heating and cracking the oil in separate chambers, while maintaining a uniform pressure and constant circulation through and between said chambers conveying the heat energy necessary for conversion and cracking in the oil itself from the heating zone to the cracking zone, and spraying said heated oil over a fixed catalyst (usually carbonaceous material) in the cracking chamber in a position above the bottom thereof so as to leave a quiet zone in the lower part of the chamber whereby any carbon formed therein will fall by gravity to the lowest part thereof, and uncracked heavy portions of the oil will collect over said carbon, withdrawing the lighter cracked products from above the catalyst and returning the said heavier liquid products into circulation to and through the heating chamber from below said catalyst."

W. E. Trent (U.S.P. 1,641,305, Sept. 6, 1927) cracks oils by distilling them in the presence of finely divided carbonaceous matter.

C. W. Wallace and H. K. Ihrig (U.S.P. 1,650,169, Nov. 22, 1927) devise "an apparatus for cracking oil comprising a still provided with a plurality of banks of tubes arranged in pairs adapted to contain the oil that is to be cracked, means for heating said tubes, endless chains of material having a catalytic action on the cracking reaction (Cu.Co.Fe.Ni.Pt.Mg.Al. etc.) arranged in each pair of tubes, and means for moving said chains longitudinally of the tubes to remove carbon deposits from the inner face of the tubes."

English Patents.

A. E. Bianchi and G. Guardabassi (E.P. 277,404, Nov. 9, 1927, and E.P. 278,041, Nov. 23, 1927) crack and hydrogenate solid and liquid hydrocarbon material in troughs provided with revolving agitators, the vapours passing through a large number of chains coated with a catalyst.

J. C. Clancy (E.P. 266,809, April 27, 1927) destructively distils carbonaceous substances, including a mixture of coal and oil, by introduction beneath the surface of a bath of molten alkali cyanide. The spent cyanide mixed with coke is revivified by using soda ash and nitrogen. *Cf.* U.S.P. 1,651,114.

The German I.G. Farbenindustrie has filed a long series of patent applications covering cracking in the presence of metals, usually employing hydrogen at high pressure and temperature. The individual patents are outlined in the following paragraphs :—

E.P. 268,796 (June 1, 1927, not yet accepted) converts hydrocarbons of high boiling point such as tars, mineral oils, etc., into compounds of lower boiling points by heating them in the presence of suitable metals, excluding those which lead to the deposition of carbon when exposed to high temperatures. Metals such as cobalt, chromium, nickel, manganese, tungsten, molybdenum and their alloys give good yields of benzine without appreciable formation of carbon and also exert a catalytic effect. Oxides or sulphides may also be used. In an example, an autoclave lined with nickel chromium alloy and containing catalysts such as molybdic acid or pyrites was charged with crude mineral oil and heated to 320° C. (608° F.).

E.P. 269,593 (June 15, 1927, not yet accepted) treats mineral oils, tar, etc., with superheated steam to obtain light oils and gases in the absence of iron or other metals which further the formation of carbon dioxide from carbon monoxide and steam. The vessel may suitably be made of copper, silver, chromium, nickel, aluminated iron or alloys.

E.P. 270,313 and 270,314 (June 22, 1927, not yet accepted) add to the metals given in E.P. 268,796 as suitable for lining cracking retorts to prevent deposition of carbon and exert a catalytic effect, a considerable number of other metals, metalloids and metallic oxides. These include titanium, zirconium, niobium, tantalum, thorium, copper, thallium, boron, silicon and their alloys, and also oxides, etc., of metals in the third to sixth groups, and of iron, cobalt and nickel.

E.P. 270,704 (June 29, 1927, not yet accepted) cracks oils in a heated column packed with a catalyst, whose inner walls are lined with material that does not give rise to carbon deposition, as certain metals, quartz and porcelain.

E.P. 271,451 (July 13, 1927, not yet accepted) carries out the cracking operation of E.P. 268,796 in the presence of hydrogen or gases yielding hydrogen.

E.P. 272,190 (July 27, 1927, not yet accepted) converts mineral oils, tars, bitumens, etc., into lower boiling products by exposure in thin films to hydrogen at elevated temperatures and pressures around 200 atmospheres, preferably in the presence of catalysts.

E.P. 272,194 (July 27, 1927, not yet accepted) forms benzine and similar oils from pastes of coal, tars and mineral oils by heating with catalysts and further exposure of the vapours, preferably superheated, to catalytic action in the presence of hydrogen or other gases at pressures running to 200 atmospheres.

E.P. 272,483 (Aug. 4, 1927, not yet accepted) prevents deposition of carbon on heating surfaces during the cracking operation by furnishing the heat from elements in motion. Oils are heated in a rotary nickel-chromium retort containing nickel-chromium balls, or in a stationary retort containing an electrically heated rotary frame of molybdenum or certain other metals. Hydrogen or other gases may be introduced.

E.P. 272,539 (Aug. 4, 1927, not yet accepted) makes provision for intimate contact between oils, tars, coal pastes, etc., that are being hydrogenated under pressure at elevated temperatures, and the hydrogenating gases, by passing the carbonaceous materials through a porous partition.

E.P. 272,556 (Aug. 10, 1927, not yet accepted) increases the yield of low boiling hydrocarbons in the cracking and hydrogenation of oils, coal, tars, etc., by circulating in a closed circuit an excess of hydrogenating gases sufficient to keep the partial pressure of the products below 10 per cent. of the total pressure.

E.P. 273,337 (Aug. 24, 1927, not yet accepted) obtains low boiling oils from mineral oils, coals, bitumen, etc., by first preparing from these materials liquid fractions with small boiling ranges, and then subjecting the fractions to hydrogenation at high temperatures and at least 50 atmospheres pressure in the presence of catalysts.

E.P. 273,712 (Aug. 31, 1927, not yet accepted) carries out the production of low boiling point oils from oils, coal, tar, etc., in two stages, first heating them under pressure in the presence of hydrogen and catalysts that assist cracking, and then heating the products with hydrogenation catalysts.

E.P. 277,273 (Nov. 2, 1927, not yet accepted) employs an apparatus made of metals not reacting with carbon monoxide for the destructive hydrogenation of oils.

E.P. 279,825 (Dec. 21, 1927, not yet accepted) carries out destructive hydrogenation and other heat treatments of oils, etc., in vessels, whose walls serve as electrical resistances.

E.P. 281,298 (Jan. 25, 1928, not yet accepted) produces aromatic compounds from mineral oils, etc., by treatment with hydrogen or gases containing hydrogen in large excess under pressure at temperatures exceeding

500° C. (932° F.). The apparatus is made from special alloys of chromium, nickel or cobalt, or surfaced with aluminium to check carbon deposition.

E.P. 282,384 (Feb. 15, 1928, not yet accepted) makes the reaction chamber for the destructive hydrogenation of oil, etc., of materials free from iron and nickel, and from copper and silver if sulphur is present, employing aluminium, or alloys containing aluminium, chromium, molybdenum, tungsten, vanadium and manganese.

E.P. 282,691 (Feb. 15, 1928, not yet accepted) produces liquid products from solid carbonaceous materials heated with high boiling mineral or other oils, adding gases not containing hydrogen, and catalysts, using high pressure.

E.P. 282,814 (Feb. 22, 1928) applies destructive hydrogenation to heavy hydrocarbon liquids at high temperatures and pressures.

E.P. 285,923 (April 18, 1928) uses hydrogenation catalysts, containing difficulty reducible oxides, of the third to fifth group, as alumina, thoria and vanadium compounds, alone or with iron or other metals of the eighth group.

F. Feige (E.P. 271,473, July 13, 1927, not yet accepted) breaks down and hydrogenates solid, liquid and gaseous fuel by subjection to high voltage electric current in an atmosphere of hydrogen, preferably in the presence of catalysts. Large yields of low boiling oils are claimed.

Internationale Bergin-Compagnie voor Olie en Kolenchemie and A. Debo (E.P. 280,734, Jan. 11, 1928) couple with apparatus for the destructive hydrogenation of coal, oil, etc., a multiple condensing system and an expansion engine for utilising the pressure of the gases.

M. Melamid (E.P. 285,879, April 18, 1928, not yet accepted) obtains liquid products from oils and tars, by spraying them intimately mixed with a finely divided catalyst and under pressure, into a heated retort by a current of hydrogen.

A. L. H. Spilker, C. Zerbe and Gesellschaft für Teer Verwertung (E.P. 277,974, Nov. 16, 1927, not yet accepted) hydrogenate and crack organic substances, including oils, by treatment with hydrogen and iodine at high pressure and temperature.

6.—*Corrosion of Cracking Equipment.*

The production of petroleum, at least in the United States, tends to crudes of higher and higher sulphur content. A large share of the oil is coming and will continue to come from California and West Texas. Many oils from these fields have a sulphur content of one to two per cent. This condition faces the cracking industry with two major problems, the protection of the cracking equipment from corrosion, and the desulphurisation of the gasoline.[67]. The corrosive qualities of the oil have not as yet been successfully overcome by preliminary removal of sulphur. The injection of

[67] Egloff and Morrell, *Oil Gas J.*, Feb. 17, 1927, 140; Dec. 8, 1927, 80. *Petroleum*, 1928, **24**, 303. Egloff, *Amer. Petr. Inst.* 1928, **9**, 227; *Oil and Gas J.*, Dec. 15, 1927, 34. Mead, *Amer. Petr. Inst.* 1928, **9**, 235; *Oil and Gas J.*, Dec. 8, 1927, 35.

chemicals to neutralise corrosive compounds has met with marked success in some cases. The re-agents most used for this purpose are lime, ammonia, sodium carbonate, and sodium hydroxide. Resistant alloys have proved useful, particularly chrome steel and chrome nickel iron, which withstand corrosion excellently, but are very expensive when used in building large size apparatus. Chromium plating of heating tubes and re-action chambers has given promising results, though there is difficulty in securing a uniform and tightly adhering film of metal. Experiments are also being made, on lining equipment with corrosion resisting materials, on gum spraying of resistant metals on exposed surfaces, and on use of nitralloys. The field is one requiring much further work.

7.—*Treatment of Cracked Distillates.*

(a) *Treating with Chemicals.*

In the desulphurisation of cracked distillates and the simultaneous removal of gum-forming constituents, an innovation of importance is the use of sulphuric acid *at low temperature*.

Halloran[68] states that with this process treating losses are nominal and the anti-knock value of the gasoline is conserved. The crude naphtha is given a preliminary caustic treatment, is washed, and dried by contact with spent acid. It is then cooled to about –5° F. (–21° C.) mixed with sulphuric acid, the sludge settled and the product washed, neutralised and distilled with fire and steam.

A comparison of the results of treating naphtha by this method and of treating with sulphuric acid without refrigeration is given below.[69]

	Ordinary Temperature.	Low Temperature.
Loss of gasoline	16·7%	4·0%
	Properties of Gasoline.	
Gravity	54·1° Be.	55·0° Be.
Doctor Test	Positive	Negative (usually)
Copper Bowl Test	Poor (84 mg. gum)	Fair (little gum)
Color	25 plus	25 plus.
Copper Strip Test	Fair (gas yellow)	Fair (gas yellow)
Sulphur	0·14%	0·09%
Unsaturates	0·17%	20%

Morrell[70] has studied polymerisation in the treatment of cracked distillates with sulphuric acid. Losses from this cause were

[68] *Amer. Petr. Inst.* 1928, **9**, 153; *Nat. Petr. News* Dec. 14, 1927, 29; *Oil and Gas J.*, Dec. 8, 1928, 36.
[69] Klemgard, *Ref. Nat. Gas. Mfr.*, May 1927, 51;
[70] *Ind. and Eng. Chem.* 1927, **19**, 794.

approximately one per cent. on Mid-Continent stock and three per cent. on California oil, while distillate from the Cushing field showed a "negative polymerisation loss" attributed to stabilisation of very light hydrocarbons usually lost. Acid treatment increased the end boiling-point of the gasoline, probably both by causing polymerisation and through the formation of alkyl sulphates. While the acid removed some unsaturated hydrocarbons, it probably would not reduce anti-knock value to a marked extent unless used in very large quantities, as for the desulphurisation of distillates from high sulphur crudes.

Chatfield[71] states that the cracked gasoline produced at the Globe Oil and Refining Co. is treated with caustic soda, settled, mixed with acid by a centrifugal pump, centrifuged to separate sludge acid, and contacted with clay, which is removed by a Sweetland press. The treated gasoline is 25 colour, non-corrosive and sun-stable, but with a slight reaction to the doctor test.

Erdely and Almasi[72] studied the behaviour of the cracked gasoline from Rumanian gas oil and from lignite tars[73] with sulphuric acid of various concentrations and with liquid sulphur dioxide. The gasolines contained large proportions of aromatic and unsaturated constituents. Very large amounts of sulphuric acid were necessary to secure maximum contraction. Liquid sulphur dioxide did not allow a clean separation of the unsaturated and aromatic hydrocarbons, but gave a water-white product of agreeable order.

Hounsell[74] successfully used copper ammonium hydroxide in the treatment of refractory cracked distillates from asphalt base crude oil. His procedure consisted of treatment with about six pounds per barrel of 66° Be sulphuric acid, washing with water, mixing with the copper solution, re-running with steam, and washing with dilute caustic soda.

A. Joseph[75] found that contact of cracked gasoline with aluminium chloride decolorised, desulphurised, and saturated it. Two hours' refluxing with five to ten per cent. of the chloride caused the separation of a tar, and gave a gasoline which after washing with 10° Be sodium hydroxide solution did not need redistillation. Naphtha containing one per cent. sulphur, from Mexican crude carrying five per cent. sulphur, produced a clear saturated gasoline with 0·01 per cent. or less sulphur which did not turn yellow or form a deposit on standing.

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[71] *Nat. Petr. News*, Oct. 12, 1927, 49.
[72] *Brennstoff-Chem.* 1927, **8**, 358.
[73] *Cf.* Varga and Erdely, *Brennstoff-Chem.* 1927, **8**, 133.
[74] *Ref. Nat. Gas. Mfr.*, March, 1928, 59; *Nat. Petr. News*, Jan. 4, 1928, 83; *Petr. Times*, 1928, **19**, 346.
[75] *Rev. Chim. Ind.* 1927, **36**, 16.

Kan[76] studied the refining of a cracked oil of sp. gr. 0·834 and iodine number 48 containing 1·15 per cent. sulphur. When this was shaken with an alcoholic solution of mercuric chloride the double compounds of ethyl and butyl mercaptans separated, with similar compounds of their higher homologues and apparently some polymerisation products. By this treatment the oil was considerably reduced in sulphur and lost its disagreeable odour. The refining and improvement in odour was also effected by heating with anhydrous copper sulphate. Sulphur dioxide escaped and most of the copper sulphate changed into copper sulphide. Refining with liquid sulphur dioxide was a further method of eliminating the disagreeable odour and producing a product stable to light and air. Ethyl sulphide was found to be very soluble in this re-agent.

Rue[77] of the U.S. Bureau of Mines reports that by careful fractionation of cracked gasoline, as in a bubble tower, undesired constituents may sometimes be concentrated in a fraction of the product, leaving the bulk of the gasoline ready for market as it comes from the condenser. In one case given as an example, it was possible to take off most of the gasoline as vapour and condense it to a water-white distillate, only a small amount being taken off as liquid, and requiring treatment for colour. With another pressure distillates the vapours came off corrosive and doctor sour, while the liquid fractions were non-corrosive and doctor sweet. In a further example the sour portions were restricted to eight per cent. of the total yield. In the work reported the average loss on acid treating was five to six per cent., though in one case it ran to thirteen per cent. It was greatest in the lighter portions of the gasoline. Short time of treatment and low temperature were advised, with the use of an alkali wash as soon as the product left the condenser, especially when re-running acid treated material.

Baxter [78] suggests the use of ozone to accelerate gum formation in cracked gasoline or shale gasoline, so that the gum-forming material may more readily be removed.

(*b*) *Treating with Adsorbents in the Vapour Phase.*

Walter Miller[79] writes: "There has been a greater extension of the use of the vapour phase filtration method in the refining of cracked gasoline, and an improvement in the technique thereof whereby the yields per ton of clay have been increased."

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[76] *J. Soc. Chem. Ind. of Japan*, 1927, **30**, 129.
[77] *Nat. Petr. News*, April 25, 1928, 48.
[78] *Nat. Petr. News*, April 25, 1928, 30.
[79] *Oil and Gas J.*, March 1, 1928, 121.

Gray[80] points out that early refining attempted to reduce the unsaturation of cracked distillates by use of large amounts of sulphuric acid or by hydrogenation. It is now known that the presence of unsaturated compounds, excepting only the diolefines, is an advantage. These are usually removed by sulphuric acid, in combination with alkali and doctor treatment and re-running, but this method is subject to losses of as much as five to ten per cent. Vapour phase refining with fuller's earth, either in connection with re-running stills or combined directly with the cracking operation, gives less loss and is more economical. Doctor treatment may be necessary in addition, though it is possible to make doctor sweet gasoline in vapour-phase refining by adding copper oxide or other materials to the fuller's earth. Use of sulphuric acid at low temperatures is efficient in removing sulphur, but causes considerable loss both of gasoline and of anti-knock value.

Henriksen[81] advises in the purification of light oil a light acid treatment, washing with water, neutralisation, and re-running with Gray Towers. If the polymer fraction from the towers is pumped back into the charging distillate, the loss by polymerisation should be about 0·8 per cent. of the gasoline produced. As the streams from the Gray Towers contain sulphur dioxide, which would react on the unsaturated and aromatic constituents of the gasoline, the gasoline should be immediately washed with sodium carbonate solution.

The Barnsdall Refineries[82] employ Gray vapour treating towers in conjunction with a Cross cracking plant. They find that when the clay no longer gives a gasoline of satisfactory colour it may be revivified by flushing with hot gasoline vapours. They have been able in this way to treat eight thousand barrels of cracked gasoline per ton of clay, against nine hundred and fifty barrels without flushing. The liquid polymers collect in the bottom of the tower and are returned to the cracking system.

The Marland Refining Co.[83] at Ponca City, Okla., uses Gray vapour-phase treating towers for Cross and Dubbs pressure distillates. The vapours from the re-run stills pass through the towers containing thirty to sixty-mesh fuller's earth, which polymerises undesirable hydrocarbons. This eliminates the necessity of nearly all of the usual chemical treatment. Increased yields, more stable product, and lowered costs are claimed.

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[80] *Nat. Petr. News*, Sept. 28, 1927, 51. (See also Mitchell, *Nat. Petr. News*, April 27, 1927, 90; *Ref. Nat. Gas. Mfr.*, April, 1927, 51.)
[81] *Oil and Gas J.*, Oct. 13, 1927, 130.
[82] Chatfield, *Nat. Petr. News*, Feb. 1, 1928, 23.
[83] C. O. Willson, *Oil and Gas J.*, May 12, 1927, 172.

Guerr and Popov[84] refined cracked kerosine distillate of yellow colour from Surachani fuel oil by passage of the vapours through a column containing fuller's earth or a Russian clay. The product was obtained in over ninety per cent. yield, was colourless, and was refined in this way at much less expense than by the customary acid alkali method.

U.S. Patents.

F. C. Axtell (U.S.P. 1,645,679, Oct. 18, 1927) employs an aromatic hydrocarbon-sulphuric acid mixture in refining oil, as in the following example: A cracked gasoline containing 0·68 per cent. of sulphur was treated with 25 lb. per barrel of a reagent made by saturating fuming sulphuric acid with benzene at ordinary temperature. The oil was separated from the acid sludge (the refining loss being about 2·56 per cent.) treated with 4 lb. per barrel of Death Valley clay, filtered and agitated with 3 lb. per barrel of 33 per cent. aqueous sodium hydroxide. The oil then contained 0.30 per cent. sulphur. It was blended with a small amount of kerosine distillate and distilled with a small quantity of caustic potash, finishing with steam. The gasoline then showed a sulphur content of 0.11 per cent.

J. C. Black, W. D. Rial and R. T. Howes (U.S. re-issue 16,679, July 12, 1927) treat synthetic or cracked gasoline to break down gum or gum forming bodies by contact with a weak solution of an alkali (as caustic soda), and then with a strong alkaline solution, subjecting the mixture of oil and strong alkali to a temperature not exceeding 350° F. (177° C.) while preventing substantial vaporization. The mixture is cooled, the alkaline solution separated, and the products mixed with a heavier hydrocarbon and distilled.

Henry Blumenberg, Jr. (U.S.P. 1,649,384, Nov. 15, 1927) presents "a process of decolourizing and deodorizing cracked gasoline with aluminium chloro-sulphate and water under agitation."

Roy Cross (U.S.P. 1,623,018, March 29, 1927) desulphurizes oil by the action of chlorine in the presence of ultraviolet light, with or without the addition of catalytic agents such as iron, aluminium, etc., or their chlorides.

Roy Cross (U.S.P. 1,654,581, Jan. 3, 1928) proposes "a process for purifying and decolourizing hydrocarbon oils, comprising the steps of bringing the oil in intimate contact by counter-flowing it with a sodium plumbite solution, the solvent being substantially immiscible in the oil, separating the oil and treating materials, and subjecting the former to the bleaching action of an absorptive agent, and maintaining the oil at temperatures above 200° F. (93° C.) and under pressure sufficient to prevent substantial vaporization during the operation."

S. J. Dickey and R. C. Wheeler (U.S.P. 1,639,988, Aug. 23, 1927) include "steps in the production of a neutral petroleum distillate from an acid treated distillate, comprising: settling and removing the coarse sludge produced by the acid treatment, passing the acid distillate through a pack of dried sand retained in a substantially closed vessel for the removal of fine sludge particles, continuing such filtration until the sand pack ceases to function by becoming internally coated with sludge,

[84] *Azerbeidj Neft. Khoz.*, Nov. 8-9, 1927, 80; *Chem. Abs.* 1928, **22**, 1033.

discontinuing the filtration, draining the free oil from the vessel, washing out the sludge with steam, and drying the sand by the passage therethrough of a current of air, thereby bringing said sand into condition for re-use without removing the sand from its operating position in the vessel."

LAZAR EDELEANU (U.S.P. 1,661,566, Mar. 6, 1928) improves gasoline in the following manner: Commercial straight-run or cracked gasoline containing constituents boiling between 130° C. and 220° C. (266° F. and 428° F.) is distilled to a terminal temperature of about 160° C. to 170° C. (320° F. to 338° F.). The distillate forms a part of the motor fuel, while the residuum is further treated with liquefied sulphur dioxide to dissolve the unsaturated and aromatic constituents. The extracted portion, freed from sulphur dioxide, is added to the distillate. The motor fuel thus produced, although containing substances boiling to about 220° C. (428° F.) has a higher average volatility than the original gasoline, and is free from substances that cause objectionable knocking in engine cylinders.

PAUL MCMICHAEL (U.S.P. 1,641,546, Sept. 6, 1927) has devised "an improved method of refining cracked hydrocarbon oils, which comprises subjecting the oil to treatment with sulphur dioxide gas, then successively subjecting the oil to treatment with an absorbent material, to a water wash, and to a treatment with a refining agent for the removal of sulphur, and thereafter distilling the treated oil."

PAUL MCMICHAEL (U.S.P. 1,655,068, Jan. 3, 1928) has developed an improved method of refining of which the following is an example: Several cracked distillates having an original sulphur content of from 0·1 per cent. to 0·8 per cent. were digested in a still provided with a reflux condenser with about one per cent. of hydrate of lime, and about 0·10 per cent. of ammonium chloride in solution in water for a period of from one to four hours at about 100° C. (212° F.). The treated oil was separated from the treating solution and agitated with about seven parts of a 75–79 per cent. solution of sulphuric acid for from one-half to two hours, the oil separated and steam distilled. Water white oils containing between 0·012 per cent. and 0·020 per cent. of sulphur are reported.

PAUL MCMICHAEL (U.S.P. 1,655,069, Jan. 3, 1928) proposes a method of refining relatively low boiling petroleum oils and distillates, which comprises subjecting the oil to treatment with caustic soda and an oxidation catalyst (hydrate of chromium, cobalt, iron, manganese or nickel) in the presence of air at ordinary temperature, separating the treated oil and subjecting it to treatment with from about one and one half to fifteen per cent. of sulphuric acid of a concentration between about seventy and eighty-three per cent. H_2SO_4, and thereafter distilling the oil with steam in the presence of a fixed alkali.

PAUL MCMICHAEL (U.S.P. 1,658,171, Feb. 7, 1928) patents "a method of refining cracked petroleum oils and distillates, which comprises subjecting the cracked oil to treatment with an aqueous solution containing sodium chromate and a greater amount of caustic soda and subsequently subjecting the cracked oil to treatment with dilute sulphuric acid."

J. C. MORRELL AND SALMEN COMAY (U.S.P. 1,627,055, May 3, 1927) cover "a method of purifying hydrocarbon oils, comprising separately subjecting

the oil to reaction with sulphuric acid, caustic soda, and copper hypochlorite and distillation in the presence of steam to remove objectionable compounds from the oil and produce a commercial product."

E. B. PHILLIPS and J. G. STAFFORD (U.S.P. 1,639,531, Aug. 16, 1927) patent an improved method of treating hydrocarbon oil which comprises subjecting the oil to refining treatment with sulphuric acid, subjecting it to distillation in a still provided with a reflux tower, passing oil vapours through the tower and introducing fresh oil into the tower in direct contact with the vapours therein in the form of an emulsion with a relatively small amount of an aqueous solution of an alkali.

ALFRED SCHWARZ (U.S.P. 1,656,990, Jan. 24, 1928) devises the process of refining hydrocarbon oil containing desirable and undesirable unsaturated hydrocarbons which comprises treating such an oil with a mixture or emulsion of sulphuric acid and saturated hydrocarbons, the sulphuric acid being in the mixture in such amount that only the undesirable unsaturated hydrocarbons are reacted upon and removed from said oil.

F. W. WEBER (U.S.P. 1,636,946, July 26, 1927) purifies oil by treatment in succession with a hypohalite as calcium hypochlorite, an agent to generate active oxygen, as sodium peroxide or a per-salt, sulphuric acid and a solution of a salt of an alkali metal hydrate and a metallic oxide of acidic character such as sodium silicate or sodium aluminate.

G. L. WENDT (U.S.P. 1,658,505, Feb. 7, 1928) covers "the method of refining hydrocarbon oils, for the removal of sulphur therefrom comprising subjecting the oils to the action of an alcoholic solution of sodium plumite."

HENRY THOMAS (U.S.P. 1,624,692, April 12, 1927) claims "the process of producing decolorized gasoline which comprises subjecting a flowing stream of a hydrocarbon containing a large proportion of gasoline and while in a vapour state to partial condensation, and intimately mixing vapours of the flowing stream with the condensate of the same stream, thereby effecting separation from the hydrocarbon of higher boiling constituents with resultant partial purification of the gasoline vapours, filtering the uncondensed vapours of the flowing stream of hydrocarbon through a body of a decolorizing material, maintaining such temperature of filtration as will permit a portion of the vapours to condense, condensing the decolorized vapours that are uncondensed in the body of decolourizing material, and conveying the condensate from said body of decolorizing material to the hydrocarbon vapours flowing toward the locus of decolorization."

ENGLISH PATENTS.

W. CARPMAEL (E.P. 276,427, Oct. 19, 1927) frees cracked oils from their more unsaturated constituents by heating with hydrated ferric chloride.

E. SCHULTZ (E.P. 277,042, Nov. 2, 1927) treats material in a cracking still and the vapours produced with purifying and converting materials such as lime, mixed with chlorides, bentonite, bauxite, etc.

CANADIAN PATENTS.

T. T. GRAY (Can. P. 273,411, Aug. 30, 1927) purifies cracked hydrocarbons in the vapour form by contact with solid absorbent material, in which polymerized compounds are deposited.

8. *Properties of Motor Fuels.*

Present day gasoline is definitely superior to that marketed in past years, particularly as regards volatility and antiknock rating. In volatility the summer gasoline surveys of the U.S. Government show a progressive improvement as indicated in the table.[85]

Date of Survey.	Specific Gravity	Gravity A.P.I.	First Drop.	20%	Endpoint.
July 1920	0·749	57·4	130°F. 54°C.	208°F. 98°C.	446°F. 230°C.
,, 1921	0·747	57·9	125°F. 52°C.	202°F. 94°C.	433°F. 223°C.
,, 1922	0·752	56·8	121°F. 49°C.	208°F. 98°C.	429°F. 221°C.
,, 1923	0·751	56·9	125°F. 52°C.	206°F. 97°C.	436°F. 224°C.
,, 1924	0·751	56·9	107°F. 42°C.	200°F. 93°C.	431°F. 222°C.
,, 1925	0·754	56·2	108°F. 42°C.	204°F. 96°C.	427°F. 219°C.
,, 1926	0·750	57·2	100°F. 38°C.	194°F. 90°C.	421°F. 216°C.
,, 1927	0·748	57·7	102°F. 39°C.	193°F. 89°C.	417°F. 214°C.

The improvement in antiknock value has been equally positive. Brown[86] has reported the results of testing forty-five samples of commercial motor fuel, which in benzol equivalent (based on straight run Pennsylvania gasoline) ranged from 10 to 50 per cent. Thirteen samples were equivalent to a 40 per cent. benzol blend or better.

Much of this improvement in antidetonating quality is due to the extension of cracking. Cracked gasoline is distinctly superior to the straight run product in this regard, because of its content of unsaturated, naphthene and aromatic hydrocarbons. Egloff and Morrell[87] found the cracked product from Seminole crude oil to have a benzol value of 25 per cent., compared with 15 per cent. for straight run gasoline from the same stock, while Spindletop cracked gasoline[88] had a benzol value of 45 per cent.

9. *Magnitude of the Cracking Industry in the United States.*

The refineries in the United States in 1927 totalled 456, with a daily crude oil capacity of 3,426,830 barrels. In operation during that year were 312 refineries whose capacity was 3,115,580 barrels. Of these, 148 operated cracking units having a capacity of 1,327,584 barrels per day, this being an increase of 146,224 barrels over 1926.

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[85] U.S. Bureau of Mines, Serial 2861, March, 1928.
[86] *Nat. Petr. News*, Jan. 25, 1928, p. 46.
[87] *Oil and Gas J.*, May 19, 1927, p. 152.
[88] *Oil and Gas J.*, Apr. 14, 1927, p. 156.

The total gasoline production for the year was 330,667,000 barrels, 101,224,000 barrels, or 30·6 per cent., being cracked product.[89] A comparison with the years 1926 and 1925 is given in the table below :—

REFINERY OPERATIONS, 1925 TO 1927.

	1927 bbls.	%	1926 bbls.	%	1925 bbls.	%
Total Gasoline Produced ..	330,667,000	—	299,734,000	—	259,601,000	—
Straight-run Gasoline ..	197,282,000	59·7	178,302,000	59·5	171,382,000	66·0
Cracked Gasoline	101,224,000	30·6	93,736,000	31·3	68,583,000	26·4
Natural Gasoline ..	32,161,000	9·7	27,696,000	9·2	19,636,000	7·6

[89] *Oil and Gas J.*, March 1, 1928, p. 120, from U.S. Bureau of Mines.

Cracking.

By R. PITKETHLY (Member).

THE continued overproduction of crude oil during 1927 had the effect of retarding expansion in the cracking section of the oil industry. This was most noticeable in the construction of new plant, as refiners apparently considered it inadvisable to increase equipment in face of the greater production of straight run spirit, combined with the steady fall in the price of motor fuel.

Another factor which assisted in the curtailment of cracking development was the cost of residual and gas oils, which at first remained high until the reduction of cracking operations set free more heavy oil, but this again was counterbalanced by the increased demand for diesel fuel. In addition to the curtailment of construction, some obsolete plants have been closed down as they could not compete with modern installations.

During 1926 the capacity of cracking plant increased by 25 per cent., whereas at the end of 1927 capacity is rather less than at the beginning of the year, but this decrease in capacity has been balanced by the increased yield of spirit obtained by modernising older units so that the total production has exceeded the production of 1926 by about 7 per cent. Over 101 million barrels of cracked spirit was made during 1927 in the United States of America. As far as figures are available, however, it appears that the increase in production of cracked spirit has not kept pace with the total production from all sources. This state of affairs will,

however, rapidly right itself as soon as market conditions improve sufficiently to balance the extra cost of production.

The improved results in the working of cracking plant and other sections of the industry are due to the rapid progress in refining technology, particularly in the application and economical utilisation of heat, and the cracking section is probably responsible for much of the increased knowledge of the subject on account of the fact that control of the conditions under which cracking is conducted is essential, and much work has been done in obtaining knowledge which is being applied throughout the refinery to obtain more efficiency and greater economy of working. The steady advance in engineering knowledge and operating experience of cracking plant have had the effect of increasing capacity of existing processes and increasing gasoline production generally.

No new processes, however, or outstanding improvements have been the cause. Rearrangement of plant, better furnace design and more knowledge of ideal temperature conditions with greater control of the distribution of heat have all contributed towards improvement both in the design of cracking plant and in its operation.

The Cross, Dubbs, Holmes-Manley, Burton and Tube and Tank processes still account for most of the production of cracked spirit to-day. These processes are all of the liquid or semi-liquid type, and vapour phase processes are practically negligible, but vapour phase cracking has received more attention recently. This attention has been stimulated by the recognition of the value of the product obtained as an anti-knock fuel for blending with straight run spirit.

Very little use has been made of vapour phase cracking processes up to date on account of the uncertainty of success, but it is of note that two of the largest independent oil companies of the United States have pooled all the patents owned by them covering vapour phase processes. Although little commercial work has been done towards the revival of vapour phase cracking for the production of anti-knock fuel, there are indications that much experimental work is being done, and its development may depend largely on consumers whether an anti-knock spirit derived from petroleum is preferable to a doped straight run product.

It is known that vapour phase spirit contains many constituents, absent in straight run spirit, which have not yet been exploited, and it is possible that vapour phase cracking may develop independently of the motor fuel demand, but meantime it appears that the process depends on this outlet for its products primarily in order to establish it on a commercial scale.

The cost of production of vapour phase spirit is higher than that of pressure cracking processes, but much research work is in progress which will no doubt have the effect of reducing costs and bringing the process into a more prominent position.

The utilisation of the large quantities of gas produced in the process is the most urgent problem, and it is probable that a synthetic industry based on this gas as a raw material is only in its infancy. At present cracked gases yield commercially some of the higher alcohols which are of particular use in certain industries, and the possibilities of development are greatest in the direction of the manufacture of non-benzoid hy drocarbon derivativesas coal products are most suitable for the production of aromatic derivatives.

The refining of vapour phase cracked spirit to make it marketable as a motor fuel is a problem which has not yet been completely solved. The refiner is faced with the difficulty of refining to a high degree for colour and odour, and at the same time he must preserve the anti-knock value of the product. In fact, the retention of its value in this respect is essential, otherwise it has no advantage over ordinary pressure distillate. In refining by standard methods the anti-knock value decreases as the colour and odour improve. Further, the product has gumming propensities greater than liquid phase spirit, and if the raw spirit is objectionable as far as colour and smell is concerned, the refined spirit is just as objectionable as far as gumming is concerned.

In order to stabilise the spirit the substances which form the gum should be removed, but these compounds have a high anti-knock value and their removal reduces its value in this respect. It is obvious, therefore, that a new system of refining is required for the treatment of these products if their value is to be maintained, unless the standards of colour and smell be reduced. Progress indicates that vapour phase refining will play a large part in the preparation of this type of spirit for the market.

The work of the Federal Oil Commission Board of the United States is beginning to take practical shape, and it is probable that its recommendations will be adopted. The suggestions made for the conservation of petroleum appear to affect only the production of crude oil at the moment, but if put in force they will affect the whole industry and no section more than cracking, for the life of the industry to-day depends on the production of motor fuel and the utilisation of inferior products, for the production of motor fuel by cracking is one of the main factors in the conservation of crude oil.

To a considerable extent crude oil and residues have taken the place of distillates for cracking purposes, and this has resulted in

an increase of the sulphur content of the cracked product. Besides being in greater quantity the sulphur compounds appear to be less reactive to the usual refining agent, sulphuric acid. Greater amounts of the reagent are required to produce a marketable product, and J. C. Morrell and G. Egloff[1] have conducted investigations on the losses due to increased treatment through polymerisation, solution and reduction of anti-knock value. They suggest that the specification standards should be reduced allowing up to ·3 per cent. of sulphur in view of the facts. They estimate that in this way a saving of about five million dollars per annum can be made in California alone.

The objection to the higher sulphur content lies in the risk of corrosion to parts of the motor, but at the same time they point out that this effect can be easily overcome by the use of ventilating devices which prevent the formation of water within the engine system.

Further investigations into the time, temperature and pressure conditions of cracking in the liquid phase have been made by A. Sachanean and M. Tilitscheyew.[2]

Their experiments show that under the same conditions of temperature and pressure the yield of spirit and kerosine rises with the time. The maximum yield of spirit for the oil under examination (Grosny Paraffin Oil S.G. ·883) is 38 per cent. to 39 per cent. The influence of pressure diminishes the yield of light products, but is useful in maintaining the liquid phase. The velocity of cracking increases five to six times for each 25° C. Condensation products are formed at the same time as decomposition products, and the residue has a higher resin value and higher specific gravity than the higher fractions of the original oil. Longer time of reaction causes the formation of asphaltenes and pitch, finally these disappear leaving coke. The velocity of cracking depends also on the character of the original oil. Different fractions from the crude showed that under the same conditions of temperature the amount of cracking became less as the specific gravity decreases.

Paraffin wax and paraffin oil after treatment with fuming sulphuric acid were cracked and no coke was obtained, besides the gravity of the residue remained unaltered irrespective of the time of reaction. As fuming acid removes aromatic hydrocarbons, it is suggested that polymerised substances and coke are produced at the expense of these compounds.

The composition of the spirit shows the effect of pressure. Increase of pressure diminishes the olefin content and naphthenes are small

[1] *Ref. and Nat. Gas. Manfg.*, March 6, 1927, 78.
[2] *Petr. Zeit.*, 1927, 521.

in amount from raw oils rich in paraffins. There is a complete absence of naphthenes in spirit obtained from paraffin wax.

These experiments lead to the conclusion that ring closing of the olefins and conversion into naphthenes plays no part in cracking.

In the patent literature concerning liquid phase or semi-liquid phase cracking, most of the work done seems to be towards improvement of existing plant, and particularly towards the prevention of the formation of carbon or coke within the cracking system.

Many processes or improvements for the refining of cracked spirit have been filed, and much work in investigating the composition of cracked products has been recorded, but only a fraction can be dealt with in this report.

The Dubbs cracking process has been improved by the addition of a "flashing" still whereby the residue from the reaction chamber is allowed to expand further with the production of a recycling stock and a heavy fuel residue. By this system more gasoline is obtained, and the gas, coke and loss reduced to about 3 per cent.

A. D. Smith and J. Perl[3] prevent the formation of carbon in an apparatus which consists of two vertical heating coils and an upright still of special construction. The raw oil is cracked in the first coil and passes into the still where the light products separate. The reflux oil from the dephlegmator is passed through the second coil for the production of more light products, and also passes into the still where separation takes place along with the products from the raw oil. It is claimed that the polymerised products of cracking are eliminated from the system before decomposition proceeds to the coking stage.

An electrical process is that of V. W. Northrup[4], who vaporises the oil to be cracked in a still and mixes the vapours with a hydrogen containing gas or natural gas. The vapour gas mixture is conducted into an ionising chamber consisting of an upright tube containing a central electrode, thence to a catalysing tube containing nickel. It is claimed that a much larger yield of spirit may be obtained by this method than by the usual pressure and heat processes and without deposition of carbon.

A. Schwarz[5] distills heavy oil from one still and light gas oil from another. The vapours from both are mixed and pass through a condenser into a receiving tank from which the uncondensed gases are recycled. The vapours from the heavy oil are mainly unsaturated and the vapours from the light oil mainly saturated. By vaporising both and cracking in contact with the gases produced

[3] U.S.P. 1,640,223.
[4] E.P. 275,120.
[5] U.S.P. 1,655,741.

in the process a rearrangement of molecules is produced which results in better yield.

W. F. Fahagher and W. A. Gruse[6] carry out the cracking of heavy oils in a cracking still, designed to prevent the formation of carbon without the use of scrapers or other mechanical means. The apparatus consists of a horizontal still with two drums situated transversely beneath it. The latter are connected to the still by large tubes and are connected to each other by a number of small tubes which are heated in a furnace. In one of the large tubes connecting to the still a gas jet is placed, and on the air lift principle the oil is caused to circulate from one drum to the still, thence to the other drum and through the heating tubes back to the starting point. By the rapid and continuous circulation of the oil produced in this way uniformity of heating and cracking results in an increased yield of gasoline with a lower make of coke.

The gas used to promote circulation is produced in the process and the operation is continuous, residuum being removed and fresh oil supplied automatically.

The method adopted by J. Primrose[7] for the heating of tubular cracking plant is typical of modern ideas on the subject. In his cracking plant a furnace is divided by a bridge wall into a combustion chamber and a heating chamber. A horizontal row of tubes is placed in the roof of the combustion chamber. These tubes are encased in cast iron blocks which absorb the radiant heat and at the same time protect the tubes from failure due to overheating. The heating chamber, protected from direct radiation, contains three banks of tubes to absorb the heat from the furnace gases. These tubes are contained in corrugated covers which increase their heat-absorbing surface. In operating the plant the oil is passed through the lower bank of tubes counter-current to the flow of hot gases, thence to the tubes situated in the roof of the furnace and finally through the uppermost bank of tubes in the heating chamber. There the oil flow is made parallel to the flow of furnace gases, which has the advantage that the temperature difference between oil and heating medium gradually diminishes, thus making it possible to subject the oil to a prolonged treatment with the consequence that a higher yield of light products is obtainable.

F. E. Wellman[8] employs an apparatus for cracking oils, in which the oil is contained in a series of vertical tubes spaced to form a circle within a heating chamber. The heat is supplied by a rotating

[6] U.S.P. 1,629,908.
[7] U.S.P. 1,626,874.
[8] U.S.P. 1,616,821.

burner to reduce the liability of overheating. The vapours formed are withdrawn through drums superimposed on several tubes.

W. H. Fletcher[9] describes a cleaning device for Dubbs' reaction chambers. It consists of a rotating drill which works upward through the lower manhole of the chamber. The drill cuts a 24-inch hole through the coke in about forty minutes. Thereafter a three-fingered spider is used. Each finger of the spider has a short length of chain with a brass disc attached. The discs break up the remainder of the coke, which falls through the manhole on to a revolving table from which it is thrown into cars standing ready to receive it.

J. E. Bell's[10] apparatus has been designed for the prevention of coke formation and consists of a horizontal still divided into compartments by baffles, which extend above the liquid level only and leave a common vapour space. Each compartment has a heating coil situated in a flue beneath the still, and these coils progressively increase in size as the temperature of the flue gases decreases. The oil flows in the same direction as the flue gases, thus the coils present a greater heating area as cracking progresses, and the oil is gradually subjected to milder cracking conditions.

C. Longhi[11] provides a novel method of applying an electric arc within a body of oil. Electrodes project through the wall of a still and a revolving disc has similar electrodes projecting radially within the still. A high-tension current which may exceed 50,000 volts causes an arc to form between the electrodes intermittently as the disc revolves.

F. W. Todt and P. Sumpf[12] produce high grade motor spirit from crude oil and its fractions, as well as from lignites and tar oils, by treating in stages of increasing temperature, the treating periods being of short duration. Highly porous substances, such as pumice stone, animal charcoal, etc., are employed to promote decomposition, and mixing of the raw material with the products is avoided. An American gas oil, for example, is cracked by passing through a tube filled with pumice at about 500° C., and the vapours are passed through a dephlegmator. The heavier constituents are recycled repeatedly until no residue remains. It is claimed that a total yield of spirit amounting to 77 per cent. may be obtained without the deposition of coke in the cracking tube.

In cracked residue fuel there is usually an objectionable amount of finely divided asphaltic or carbonaceous material.

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[9] *Nat. Petr. News*, Sept. 21, 1927, 171.
[10] U.S.P. 1641, 941.
[11] E.P. 275,281.
[12] E.P. 267,364.

The Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij[13] patent is a method for the separation of this finely-divided material. It consists of acting on the hot fuel with dilute sulphuric acid (33 per cent.). The deposit is separated as a granular coke, leaving the oil with about 1·0 per cent. of suspended matter.

A new process by E. R. Wolcott[14] consists of a number of tubes mounted within a still. One arm of each tube projects through the shell of the still into a combustion chamber provided with a sparking plug or other ignition device. Each combustion chamber has an oil or combustible gas supply and an air supply, or the proper combustible mixture may be supplied through one tube.

In carrying out the process a charge of oil is admitted to the U tubes and an explosive mixture to the combustion chambers. The explosive mixture is ignited, producing a temperature and pressure sufficient to produce decomposition of the oil which expands into the still and vaporises. The vapours pass through a dephlegmatory and are finally condensed.

L. de Florez[15], in a paper on vapour phase cracking, explains how liquid phase processes have developed, on account of the desire for a product which resembled straight run spirit. He says that vapour phase cracking may be carried out up to 750° C., yielding from 23 per cent. to 30 per cent. of gasoline in one passage through the plant. The chief problem encountered is that relating to efficient heat transfer, and the only method is to pass the vapours through tubes of small bore at a high velocity. An account of a plant built for the New England Oil Company is given. The cracking tubes are 1 in. in diameter, bent in the form of a hairpin to facilitate removal or replacement. The plant consists of eight units, each capable of processing 125 barrels per day. The average output was 830 barrels per day over a period of some months, with an idle time of 17 per cent. for all purposes. The plant paid for itself in five months. The charging stock is an overhead distillate and no coke is deposited. The stability of the spirit is not high and is blended at once with straight run product.

The treatment of cracked spirit has given much trouble, and many new methods of treatment have been put forward, a few of which may be mentioned.

J. C. Black[16] describes a method for dealing with acid treated cracked distillates. The material is neutralised with weak alkali and separated. A strong alkaline solution is then added and the mixture treated to about 350° F. with continuous agitation. The

[13] E.P. 270,274.
[14] U.S.P. 1,654,711.
[15] *Refiner*, 1928, 1., 71.
[16] U.S.P. 16,679. *J. Inst. Petr. Techn.*, 1927, 13, 193*a*.

alkali is separated and the treated oil mixed with crude oil containing gasoline. Distillation produces a refined motor fuel, leaving gums and polymers in the crude oil residue.

P. McMichael[17] proposes to refine cracked spirit by vigorously agitating with SO_2 gas, then filtering through a bed of absorbent earth or such material. After filtration the oil is washed with water or dilute alkali. If further purification is necessary hypochloride or a redistillation may be given.

For the treatment of cracked gasoline containing objectionable amounts of sulphur R. Cross[18] utilises a tower down which a solution of metallic salts flows counter current to a stream of the oil. The treating solution may contain salts of lead, copper, antimony, zinc or manganese which have the power of combining with the sulphur present in the oil. The most satisfactory of the solutions are sodium plumbite and copper sulphate, preferably in a neutral or weak alkaline condition. The oil may be finished by passage through a second tower containing bentonite or fuller's earth. The process may be used in cracking plant towers for vapours under pressure or otherwise.

Improvements have been made in Gray's vapour phase refining process. A great advance has been made in the method of operating the plant with a great saving in refining cost. In the old method of running, when the colour of the spirit fell off, the process was stopped and the earth was reactivated. By this method about 1,000 barrels of spirit per ton of earth were treated. It is now possible to prolong the life of the earth to such an extent that over 8,000 barrels of spirit per ton of earth may be treated continuously.

This greatly increased efficiency has been made possible by the discovery that the polymerised substances absorbed by the earth may be flushed out by means of the hot vapours of the cracked spirit. By releasing the pressure on the receiver for the polymerised oil, the vapours are caused to pass downward and wash out the polymers from the tower into this receiver. After flushing, pressure is restored, the vapours pass through the condenser normally, and the earth has recovered its refining power. The method can be used repeatedly. On the old basis the cost per barrel amounted to 0·5 cents per barrel, whilst the modified process costs ·00625 cents per barrel.

H. P. Rue[19] advocates the careful fractionation of cracked spirit. Using a thirteen plate column and cracked pressure distillate, he found that 30 to 40 per cent. was of good colour and the remainder

[17] U.S.P. 1,641,546.
[18] U.S.P. 1,654,581.
[19] *Nat. Petr. News*, 20, 17.

only required treatment. An apparent segregation of the sulphur compounds occurred. If the total yield of spirit were taken overhead the distillate was corrosive and sour, but if temperatures were controlled so that part of the spirit were taken overhead and part from the plates and these mixed later to give the total spirit yield, it was possible to obtain a sweet and non-corrosive product.

In another case where the overhead product was always doctor sour, controlling the temperatures and drawing off in three different streams, had the effect of reducing the sour fraction to 8 per cent.

Some interesting points regarding gum content of various fractions were noted. In one case the 30 to 40 per cent. fraction formed more gum on standing than all the other fractions combined. It is, however, not always the same fractions in different cracked spirit which contain the greatest amount of gum. It must not be assumed that it is possible to eliminate gums entirely, but it was found, by controlling temperatures and the amounts of the different streams, that one of the streams contained more gum than the others, and it was possible to vary the gum content at will by altering conditions.

It is advisable that each refiner should study the crude product he is running and find out which parts of the gasoline require refining by different methods. The volume of product which must be treated would be reduced considerably.

J. C. Morrell[20] suggests that polymerisation is not the cause of loss when cracked spirit is treated with sulphuric acid. An increase in end point of acid treated gasoline was observed in agreement with the results of other workers. This increase was found to depend on the concentration of the acid and amount used. Polymerisation supplies only a partial explanation, and it is suggested that the increase is largely due to the decomposition, on distillation, of dialkyl esthers of sulphuric acid, yielding high boiling substances.

R. A. Baxter[21] suggests that the gums formed in cracked gasoline are caused by oxidation rather than polymerisation. Samples were treated with ozone to accelerate the formation of gum. The gum may thus be eliminated without destroying the anti-knock value of the product.

J. S. S. Brame and T. G. Hunter[22] contribute a valuable paper on the composition of cracked distillates. The difficulty of ascertaining its composition lies mainly in the fact that methods of isolating the different classes of compounds are very unsatisfactory.

[20] *Ind. Eng. Chem.*, **19**, 794.
[21] *Nat. Petr. News*, **20**, 17, 30.
[22] *J. Inst. Petr. Tech.*, 1927, **13**, 794.

This research, therefore, was primarily undertaken with the object of investigating possible methods. The first line of attack was that of selective solution in organic solvents; but although distinct differences exist in the solubilities of different hydrocarbons in certain solvents, no satisfactory degree of separation was obtained.

Chemical methods of separation, using mercuric chloride and acetate, were tried without satisfactory recovery of the hydrocarbons. Bromination, at low temperature, gave exceptionally good yields on subsequent distillation with copper-zinc or aluminium-mercury couple. Successful separation of the unsaturated compounds left the aromatics free to be removed by sulphation, then attention was directed to the separation of the naphthenes and paraffins. This was accomplished by fractional distillation in the presence of a third component, the best liquid for this purpose being aniline.

Another paper of interest to refiners, particularly in connection with cracked spirit, is that of W. R. Ormandy and E. C. Craven[23] wherein they record the results of an investigation on the action of strong sulphuric acid on unsaturated compounds. They find that olefins or alcohols containing three or more carbon atoms form saturated hydrocarbons which separate from the mixture and highly unsaturated hydrocarbons which remain in acid solution. Alcohols and olefins derived from open chain paraffins yield open chain paraffins, whilst alcohols from cyclic paraffins yield cyclic and polycyclic paraffins. When olefins and aromatics are togther acted on with cold conc. H_2SO_4, some of the aromatics join with the separated paraffins.

[23] *J. Inst. Petr. Tech.*, 1927, **13**, 844.

The Principle of the Koenigsfeld System of High Vacuum Distillation and Two-Phase Evaporation.*

By M. L. Steinschneider (Member).

The Steinschneider high vacuum distilling plant was up to the present provided with a horizontal cylindrical still similar in construction to a Cornish single-flue boiler.

The still is stayed internally to prevent collapse through atmospheric pressure. The fire gases are led firstly through the internal flue and thence outside and along the shell into the stack. Distillation is effected under an absolute pressure of 20–60 mm.Hg. and with the aid of steam.

* Paper received June 10th, 1928.

The mixture of oil and water vapours is conducted through a series of dephlegmators, at least two, generally three, in such a manner that from the last dephlegmator only the fixed gases, the uncondensed water vapours and the lightest products reach the barometric condenser, where they are cooled and condensed by contact with cooling water.

Within recent years the following improvements have been made and thoroughly tested.

1. *Improvement in Firing. Prevention of Cracking.*

The raw material is no longer heated in the still proper, but in a tube still, through which it is circulated at a high velocity, about 1½ m. per second, by means of a circulating pump.

The raw material passing through the tubes of the tube still is under a pressure of 1½ atmospheres, or more, so that it cannot evaporate in the tube still. Owing to this and to the rapid circulation of the material whilst being heated, the separating out of coke in the tubes is impossible, even if the supervision of the apparatus during operation is deficient.

Actually, after twelve months' operation, the tubes in a plant distilling a heavy crude residue down to hard asphalt were bright, and cleaning was unnecessary.

The pressure in the tube still is maintained at the desired height by means of a throttle valve placed behind it. The charge, heated uniformly in the tube still, is evaporated in the cylindrical still, after having passed through a gas separator, the purpose of which will be explained later.

The cylindrical still, surrounded only by the hot gases which come from the tube still, is subjected to relatively low temperatures only, and for this reason there is far less risk of deformation due to atmospheric pressure than in stills with direct external firing. The internal staying of the still can therefore be of smaller dimensions and so arranged that cleaning can be easily effected.

In externally fired vacuum stills, the type mostly used in America, there is always the risk of the deposition of coke owing to the almost unavoidable partial overheating. This results in burning through of the shell and collapse through atmospheric pressure. In such stills, moreover, the stock is liable to be cracked and the quality of the distillates lowered in consequence.

2. *Enlargement of Evaporating Surface. Prevention of Mechanical Entrainment of Undistilled Constituents.*

The interior of the still is, as proposed by Neumann, provided with a tray extending practically over its total length and width.

The heated raw material is first discharged on this tray and then overflows into the still; by this means the evaporating surface is nearly doubled.

A mechanical entrainment of undistilled constituents is thus almost entirely prevented. The products of distillation can consequently be refined more cheaply and with less loss. In the case of some oils subsequent treatment of the distillates with sulphuric acid and lye or clay is altogether unnecessary.

3. *Complete Separation of Unsaturated and Detrimental Products. Better Fractionation. The Principle of Two-Phase-Distillation.*

The vaporization of the heated charge is carried out in two entirely separate phases. Located between the tube still and the cylindrical still is a gas separator, which is kept under a lower vacuum, or in other words, under a higher absolute pressure than the cylindrical still.

The absolute pressure in this gas separator is kept so high that only the light, unsaturated products and the permanent gases can escape therefrom, so that the evaporation of the desired, saturated products does not take place here, but in the cylindrical still.

The raw material thereupon proceeds from the gas separator into the cylindrical still, and only there, in consequence of the lower absolute pressure, does evaporation of the heavy, saturated products take place. This arrangement enables an almost perfect separation of the unsaturated products ("stink oils"), which is of the utmost importance for the subsequent refining of the oils.

The separation of the stink oils in so complete a manner is not possible in the distillation systems hitherto employed, as these products accompany the desired products into the fractionating equipment and there remain in contact with each other for too long a time, and in part, condense together, in even the best fractionating apparatus.

These unsaturated products, which polymerise and oxidize, require for their removal large quantities of sulphuric acid and heavy losses result from the formation of acid resins.

4. *Better Evaporation, due to Intensive Mechanical Circulation, even when Distilling without Steam. Perfect Action of the Vacuum owing to the Elimination of the Liquid Column above the Evaporating Surfaces.*

In direct fired stills the vacuum existing in the evaporation space is not fully effective during the evaporation proper. The vaporizing liquid particles are under the pressure of the liquid column above them, the height of which is about one metre in stills

with internal flues and two metres, or more, in underfired stills without internal flues. An oil column one metre high is equivalent to a mercurial pressure of about 55 mm. Consequently, evaporation is not proceeding under the absolute pressure indicated by the vacuum meter for the vapour space, but under this pressure plus the pressure exercised by the liquid column.

The higher the vacuum under which distillation is to be effected, the more this condition is aggravated. When the vacuum in the vapour space of an underfired still indicates, for example, a pressure of 3 mm. Hg., the formation of the oil vapour bubbles is taking place under a pressure increased by 110 mm. Hg. owing to the oil column of about two metres existing above the vaporizing particles. Thus, vaporization is not proceeding under a pressure of 3 mm. Hg., but of 113 mm. Hg. The evaporation temperature, therefore, does not correspond to a pressure of 3 mm., but 113 mm. Hg., and it is consequently proportionately higher.

This disadvantage is entirely eliminated in the new system. Evaporation in the gas separator as well as in the still always takes place from the surface of the liquid, therefore from a thin layer, because all the particles of the liquid are driven to this surface by the positive and intensive circulation between tube still and cylindrical still. This movement is greatly intensified when steam is used during distillation.

5. *No Decomposition, even when Distilling Down to Hard Asphalt.*

The heating of the raw material to the end-point is not effected by a single passage through the tube still; it is conducted through the tube still repeatedly and on each occasion the temperature is only so gradually raised that all overheating is avoided. Cracking of the raw material is consequently precluded and the heaviest fractions are won as distillates (overhead distillates) without any decomposition; they are, moreover, in consequence of the total absence of decomposition, entirely free from tar. In paraffinous distillates the paraffin is quite amorphous, and being free from tar these distillates can be dewaxed by the aid of centrifugal separators without preliminary treatment. Re-distillation of the dewaxed oil yields excellent lubricating oils which, as a rule, need no subsequent chemical treatment.

The asphalt is absolutely free from coke and is a suitable material for asphalt paving, for the manufacture of roofing felt, for insulating purposes, etc.

When the raw material is only passed once through the tube still (single flash distillation) heating to the end temperature takes place immediately. This method possesses, with the simultaneous

vaporization of products which show great differences in their molecular weights, many advantages. The partial tension of the heavy oil vapours is increased by the light oil vapours and their boiling point consequently lowered. As the molecular weights of the heavy fractions differ very little from each other, this advantage is not present when distilling heavy oils from heavy residues. On the other hand, with single heating to the end temperature, the risk of overheating the raw material is far greater, with the result that tar, the boiling point of which differs very little from that of the heaviest fractions, also distils over with the other products, whereby refining is rendered more difficult and great losses entailed.

6. *Easy Supervision. Small Outlay for Repairs, which are Quickly and Readily Effected.*

As only the tube still is subject to wear, any necessary repairs can be carried out expeditiously and without long interruption of the operations. The cost of such repairs is small, because it is only a question of the replacement of a few tubes. In the distillation of heavy residues down to hard asphalt no wear of tubes could be detected after one year's service.

7. *Suitability of the New Method of Distillation for the Continuous Treatment of Large Quantities, with Sharp Fractionation.*

The treatment of large quantities is effected continuously in several units, arranged one after the other, and forming one battery. In each unit evaporation is carried out in two phases, the decomposed products from the corresponding evaporator being separated out, in the manner described. As at least two fractions are formed in each unit, the distillates are, if, say, six units are employed, divided into twelve fractions. By proper regulation of the fractions the desired end products can be obtained without subsequent re-distillation.

8. *Distillation under Highest Vacuum Employing Small Air Pumps.*

By the interposition of the evaporator a very high vacuum can be generated in the cylindrical still with a comparatively small air pump. When distillation is to be effected under a very high vacuum, a two-stage air pump having two separate air pump cylinders is employed. One of these draws the uncondensable gases from the evaporator, which is under a higher absolute pressure than the still.

In all other systems of distillation the lightest products and the uncondensable gases are formed simultaneously with the oil vapours in the still and must consequently be pumped out under the lower absolute pressure of the still.

In the new system, each stroke of the piston withdraws a large amount of uncondensable gases from the evaporator.

Only small quantities of uncondensable gases, which are formed in the still, are drawn off by the second air pump cylinder and delivered into the suction piping of the first air pump cylinder.

A vacuum to 4 mm. Hg., or less, can, therefore, be readily attained and maintained with relatively small air pumps.

9. *Adaptability of the Plant for Distillation With or Without Steam.*

The condensing apparatus are so arranged that they can be operated with steam and high vacuum, as well as with extreme vacuum and without steam. Working can be changed from one method to the other whilst the plant is in full operation.

The evaporator, the tray inside the still and the still itself are fitted with steam distributing pipes, so that steam can be injected into all the said apparatus or into any of them as required. If distillation is to be effected with an absolute pressure not exceeding 20 mm. Hg., steam is injected into the evaporator only, but not into the tray and the still.

The choice of the method of working will depend upon the nature of the raw material which is to be distilled. In most cases, distillation with steam and an absolute pressure of about 25 mm. Hg. has proved recommendable.

10. *Easy and Continuous Control of the Distillates.*

As in the former Steinschneider system, the distillates are pumped from the cooling apparatus and delivered visibly into the receiving box. Thus, samples of the distillates can be taken at any time, the working process is always under control and the attendance simplified.

In high vacuum plant which is not provided with this equipment control is troublesome, as the distillates have to be collected in closed tanks, which are also under vacuum. These tanks are often a source of leakage and render it difficult to maintain the vacuum.

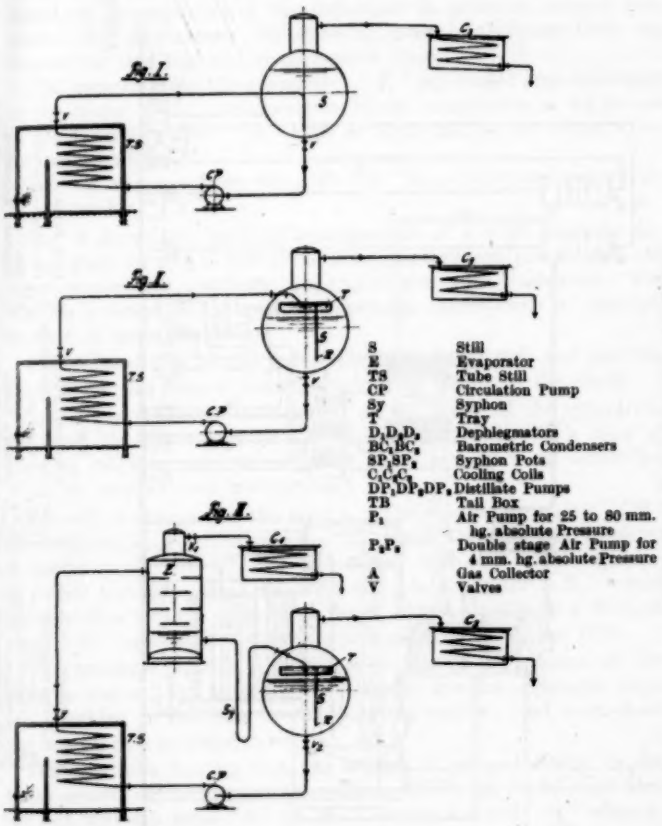
The attached diagrams will serve to illustrate in detail the method of working of high vacuum plant of the most modern system.

In Fig. 1 "S" represents the cylindrical still, from which the circulation pump "CP" draws the raw material and delivers it through the direct fired tube still "TS"; the material then passes through the throttle valve "V" and returns into the cylindrical still. The temperature of the raw material is gradually raised

each time it passes through the tube-still, and overheating and cracking are thus avoided.

Two Stage Vacuum Distillation.

(Patent.)



In Fig. 2, which in principle shows the same arrangement as Fig. 1, the tray "T" inside the still is indicated, and from this the material which is not evaporated flows into the still through the overflow pipe "R."

Fig. 3 shows in principle the arrangement of a two-phase distilling plant. The oil drawn out of the still "S" by the circulation pump "CP" is, as in the arrangements above described, pumped through the direct fired tube-still "TS" and, after passing the

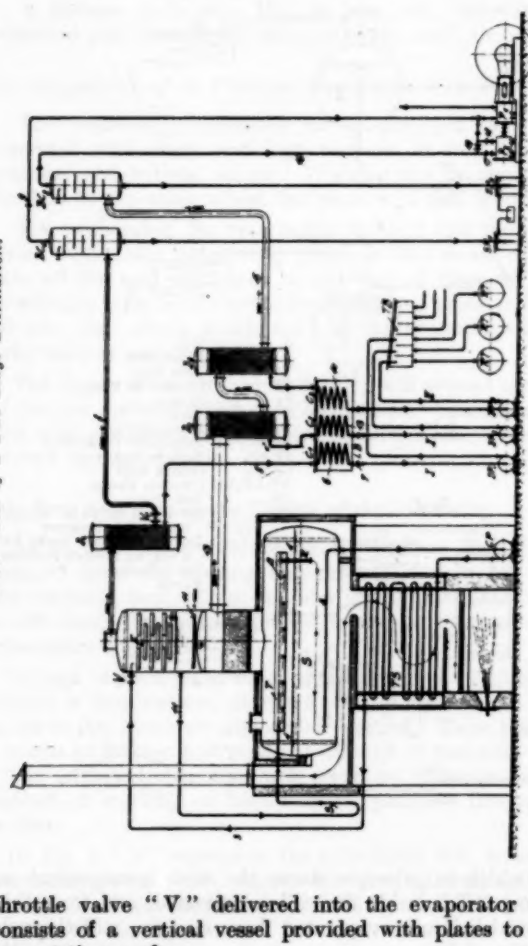


FIG. 4.

throttle valve "V" delivered into the evaporator "E," which consists of a vertical vessel provided with plates to increase the evaporating surface.

The oil not vaporised in the evaporator flows through the syphon pipe "Sy" into the tray inside the cylindrical still and thence into the still itself. The absolute pressure in the still is lower than in the evaporator; in the still, for example, it is 20 mm. Hg, in the evaporator 65 mm. Hg.

The height of the syphon "Sy" is so great that suction of the liquid, in consequence of the difference in pressure, cannot take place. By this means the drawing over of vapours from the evaporator into the still is prevented.

The vapours from the evaporator "E" are cooled and condensed in the cooler "C1"; the pressure in the evaporator is, by means of the throttle valve "Vl," kept so high that no oil vapours can escape therefrom.

The oil vapours from the still "S" are condensed separately in the cooler "C2."

Fig. 4 shows the general arrangement of a high vacuum distilling plant in which the whole fractionating equipment and the most important auxiliary apparatus are also indicated. The relative location of the various apparatus corresponds in principle to that in actual practice.

The tube-still is placed below the cylindrical still and the flue gases from the former ascend around the latter to the stack.

The gas separator is mounted on the dome of the cylindrical still, and the lower part of the dome is provided with a layer of Raschig rings in order to separate out every trace of undistilled particles carried over mechanically.

The still is charged to the level 1. The circulation pump "CP" draws the oil down through pipe "2" inside the still and circulates it continuously through the direct-fired tube-still "TS," whence it passes through pipe "3" into the gas separator "E," which consists of a vertical cylindrical vessel, closed tightly by a division plate "4" against the dome-shaped upper part of the still.

The pressure in the tube-still is regulated by means of the throttle valve "V" in pipe "3." Inside the gas separator trays are provided to increase the evaporating surface, and over these the heated raw material flows.

The products leaving this gas separator proceed firstly to the water-cooled dephlegmator D1. Those which are condensed here are led through pipe "5" to the water-cooled coil "6," whence, after passing through look-box "7," they are drawn off by pump "DP" and delivered visibly into the receiving box.

The vapours not condensed in dephlegmator D1, *i.e.*, the permanent gases, and perhaps water vapours, are led through pipe "8" to the barometric condenser "BC1." Water is injected into the

barometric condenser, whereby the last condensable products are precipitated and the permanent gases cooled.

Through piping " 9 " the permanent gases are drawn off by an air pump.

In order that only the lightest products and only unsaturated products—but no saturated heavy fractions—shall be distilled out of the gas separator, the pressure in the separator is regulated by a throttle valve " Vl." If the distillate pump " DP 1 " delivers heavy products, the pressure in the gas separator is increased, by throttling the valve " V1," until only unsaturated products are distilled off.

The raw material from which the gases have been separated is accumulated in the gas separator up to level " 10." By means of the steam spray pipe " 11," steam can be introduced, if necessary, in order to complete the expulsion of the gases from the oil.

The raw material is then returned through piping " 11 " and syphon pipe " Sy " to the tray " T " inside the still, which forms the evaporating surface " 12." In consequence of the lower absolute pressure prevailing in the still the evaporation of the heavier hydrocarbons now sets in. The material not evaporated in the tray flows through overflow pipe " R "—which is expanded at the top of the shape of a funnel—into the still and forms there the second evaporating surface " 1." It then traverses the whole length of the still and passes again through pipe " 2 " to the circulating pump " CP," whereupon the cycle is repeated until the raw material is reduced to the desired residuum.

Both the tray " T " and the still are provided with steam spray pipes by means of which, singly or together, steam can be introduced.

The oil vapours flow from the still through piping " 13 " successively into the dephlegmators " D2 " and " D3," from which the condensed fractions flow to the water-cooled coils " 13 " and " 14 " and thence through look-boxes to the distillate pumps " DP2 " and " DP3," which deliver the fractions visibly into the receiving box.

The products not condensed in the last dephlegmator " D3 " are still partly composed of light fractions, chiefly unsaturated hydrocarbons and uncondensable gases which develop only under the lower pressure in the still. These flow through piping " 15 " into a second barometric condenser " BC2," from which they are, after having been cooled by injected water, drawn off through pipe " 16 " by a second air pump cylinder " P2."

From this drawing the arrangement of the two-stage air pump and the location of the suction pipes can also be seen.

When steam is used, only an absolute pressure corresponding to the temperature of the cooling water can be attained—60-20mm.

In this case steam is admitted into the gas separator, tray and still. In most cases, however, the separator is not supplied with steam, but only the tray and the still. In distilling with the aid of steam in the evaporator and the still, cooling water is injected into both barometric condensers "BC1" and "BC2," the air pump "P2" is preferably shut off by closing valves "17" and "18," and valve "19" opened, so that both barometric condensers are evacuated through piping "9" and "16" by the air pump "P1," the gases removed being discharged into the atmosphere through piping "19."

Continuous working Two Stage Distillation with three units.
(Patent.)

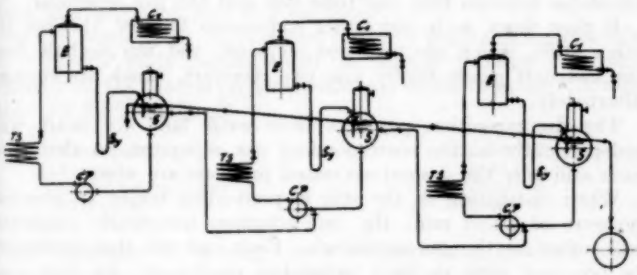


FIG. 5.

S Still — TS Tube Still — Sy Syphon
E Evaporator — CP Circulation Pump — C_1 Cooling Coils

When it is desired to distil under an absolute pressure lower than 20 mm., for example, 3 mm. measured in the still, no steam is supplied to the still. Two methods of operation are then possible, viz., the gas separator also is, or is not, supplied with steam. In both cases air pump cylinders "P1" and "P2" are in operation, valves "17" and "18" open, valve "19" closed. The barometric condenser "BC1" is evacuated by air pump "P1," the barometric condenser "BC2" by air pump cylinder "P2," which delivers the gases drawn off into the suction piping "9" of the barometric condenser "BC1."

No cooling water is injected into the barometric condenser "BC2," because the still is not being supplied with steam. Cooling water is only injected into the barometric condenser "BC1" when distillation in the gas separator "E" is being effected with the aid of steam.

In the case of barometric condensers in which no water vapour is to be condensed, it is advisable to inject gas-oil as a cooling

medium, in order to cool the uncondensable gases and to free them from the last traces of entrained oil particles.

The possibility of altering the method of working during full operation, that is, of changing over from working with steam to working without steam, and of utilising a high vacuum limited only by mechanical difficulties invest the new plant with advantages which are not attainable by any other.

Fig. 5 graphically represents a continuous two-phase distilling plant, consisting of three units. Each unit comprises the same apparatus as in Fig. 4, but only the main items are shown in order to illustrate the grouping as distinctly as possible.

The raw material is charged into the first highest still and circulates between this, the tube still and the gas separator.

It then flows, as in any other continuous battery, through the other stills, which are arranged stepwise, and the asphalt from the last unit passes finally into two receivers, which are emptied alternately.

The decomposition products from each unit are dealt with independently in the corresponding gas separator, so that from each still only the desired saturated products are won.

When distillation in the still is proceeding under an absolute pressure of 20-50 mm. Hg, one common barometric condenser will suffice for the gas separators. Each still will then preferably be provided with its own barometric condenser. In that case, one air pump would be sufficient for the whole battery, but it is more advantageous to use two, one to evacuate the gas separators, the other to evacuate the stills.

When distilling under an absolute pressure lower than 20 mm. one air pump is provided for the common baromteric condenser of the gas separators and separate pumps are provided for the condenser of each still.

Heavy Distillates, Fuel Oils, Asphalts, and Residues.*

By F. H. Garner, Ph.D. (Member).

The variation of the sulphur content of carburetted water gas as a result of using oils of different sulphur contents has been reported in *J. Usines Gaz* (1926), **50**, 407, by an anonymous author.[1]

The oils had sulphur contents varying from 0·27 per cent. to 2·8 per cent., and the increase in sulphur content of the water gas after carburetting is reported as increase in sulphuretted hydrogen and increase in carbon bisulphide.

* Paper received August 2, 1928.

[1] *Chem. Abs.*, 1927, **21**, 484.

The increase in sulphur content of the water gas, due to the use of oil of 0·27 per cent. sulphur content, was found to be 0·04 gm. sulphur per cubic metre of carbon bisulphide, and 0.4 gm. sulphur as sulphuretted hydrogen. With oil of 2·82 per cent. sulphur the corresponding figures were 0·149 gm. per cubic metre as carbon bisulphide, and 4·4 gm. per cubic metre as sulphuretted hydrogen.

Specifications for Domestic Furnace Oil are discussed by W. T. Ziegenhain[2], who suggests the following :—

Maximum thermoviscosity	750
Flash point, Tag open	170° F.

In addition to these requirements the oils should be free from water and sediment, and of good odour.

As the result of an examination of thirty grades of furnace oils, H. J. Struth[3] finds that although the specific gravities vary from 0·80 to 0·89, the general physical constants as shown in the following table, are fairly uniform.

Flash point	130–190° F.
Viscosity	33–40 secs.
Initial boiling point	370–410° F.
End point	590–630° F.

The difficulty of burning heavy residues from cracking plant flashing operations is dealt with by G. C. Chatfield[4].

A circulation of four to five times the amount of fuel consumed is suggested, and the use of steam or gas oil connections at points where the line may become blocked.

Brunler, in *Industrial Chemist* for May, 1927[5], described the latest developments of the Brunler flame. Essentially this consists of a water cooled burner which is fed with fuel under pressure and compressed air in theoretical quantities. For steam raising the combustion takes place surrounded by water, and a steam-gas mixture of approximately 50 per cent. steam and 50 per cent. carbon dioxide and nitrogen is generated. It is stated that the flame has been successfully used for concentration of sulphuric acid, waste sulphite liquors and other chemical liquors.

The theory of ignition and combustion processes in Diesel engines is discussed by Sass.[6] Diesel himself assumed that the fuel was gasified before ignition occurred in the Diesel engine. The ignition point of the oil gases from four Diesel oils were found by Woller and

[1] *Chem. Abs.*, 1927, **21**, 2791.
[2] *Chem. Abs.*, 1927, **21**, 2791.
[3] *Chem. Abs.*, 1927, **21**, 1539.
[4] *Ind. Chem.*, 1927, **3**, 215.
[5] *Zeit. Ver. deut. Ing.*, 1927, **71**, 1287.

Ehnicke to show no definite relation to the ignition points of the oils as determined in the Moore apparatus. The ignition points of the oil gases ranged from 614–661°, whereas, the ignition points of the oils themselves range from 240–468°. It was further confirmed by tests in a hot bulb engine that, if the fuel must be gaseous before ignition occurred, that no ignition could have taken place down to one-quarter load, whereas actually ignition was regular and certain at all loads. It is, therefore, improbable that the oil is gasified before ignition, and a theory of the mechanism of combustion is suggested by Sass. A layer of oxygen surrounds the liquid particle and superoxides are formed which are only stable within a small range of temperature and pressure. Outside these limits the compounds break down and combustion of the fuel particle occurs. The importance of the "ignition lag," the period of time between injection and ignition, in reference to the proper rate of compression is discussed. No part of the combustion chamber should be above the cracking temperature of the fuel, as otherwise cracking occurs with consequent incomplete combustion, giving a sooty exhaust.

The American Society for Testing Materials in the last issue of *Standards* (1927) gives specifications for a large number of materials containing asphalt for roofing and grouting purposes.

Definitions of terms relating to materials for roads and pavements are also given, in which "bitumen" is the generic term, and "asphalt" the term applied to natural and petroleum asphalts (p. 519).

Tentative methods for sampling and for carrying out the various tests on asphalt are also described.

The terminology methods of testing and standards of so called "asphalt tars" in the Soviet Republic are discussed by Sakhanov and Sherdeva.[7]

By *asphalt tar* is meant the partly solid or solid residue from petroleum. *Oxidised asphalt tar* is applied to asphalts produced by blowing with air, *sulphonated acid tar* to asphalts produced by sulphonation, and *regenerated acid tar* to products formed from acid residues. *Asphalt* includes natural mixtures of limestone with asphalt tars and also artificial mixtures. The methods of testing comprise determinations of ash, softening temperature, permeability, flash-point, extensibility and density.

E. E. Graefe[8], finds that asphalt has no latent heat or definite melting point as shown by the chilling curve and heat of solution. The quantity of heat necessary to render asphalt liquid is, therefore, dependent only on the specific heat of the asphalt. Coal tar

[7] *Chem. Abs.*, 1927, 21, 4059.
[8] *Chem. Abs.*, 1927, 21, 1881.

pitch does show a low heat of melting owing to the presence of crystalline hydrocarbons.

Nellensteyn[9] develops further his theory of the constitution of asphalt. Asphalt is a highly protected carbon oleosol containing three principal constituents—the carbon particles, the protective substance, and the medium. The first two form the asphalt micelles and are surrounded by the medium. The behaviour of the asphalt in solution is explained on this theory as follows:—Where the micelle is insoluble in the solvent but is not itself broken down, as in the determination of asphaltenes by means of petroleum ether, reversible flocking occurs. The flocking depends almost entirely upon the surface tension between micelle and medium. Liquids with a low surface tension as, for example, petroleum ether or ethyl ether, are flocking agencies, those with a higher surface tension, as for example, benzene, have a solvent action. Carbon tetrachloride has a surface tension of 24/25 dynes per sq. cm. which corresponds to the critical surface tension for producing flocking, and in this fact perhaps offers an explanation of Richardson's carbene test. If the micelle itself is destroyed, then irreversible flocking occurs.

Nellensteyn has also shown[10] the relation between wetting ability and surface tension of an asphalt. The surface tension of oxidised asphalt was found to be lowest, petroleum asphalt intermediate, and coal tar highest of all.

Marcusson[11] describes a new method of estimating asphalts in mineral oils in which the asphalt is precipitated as a double compound with iron chloride. Five grams of the oil dissolved in 50 c.c. of ether, is treated with 5 c.c. of a five per cent. ether solution of ferric chloride. The precipitate is freed from oil by washing with ether and then dissolved in chloroform. Hydrochloric acid is mixed with the chloroform solution, dissolving the iron chloride, leaving a chloroform solution of asphaltenes. After distilling off the chloroform the percentage of asphaltenes in the oil may be determined.

Marcusson[12] claims that this method of estimation has the advantages of simplicity, and gives an absolute method of estimation. The percentages found by this method are much higher than those obtained by the so-called normal benzine.

An interesting paper on the recovery and examination of asphalt extracted from asphaltic paving mixtures was given by Bateman

[9] *Zeit. Angew Chem.*, 1927, **40**, 1195.
[10] *Chem. Abs.*, 1927, **21**, 2792.
[11] *Chem. Zeit.*, 1927, **51**, 190.
[12] *Chem. Abs.*, 1927, **21**, 1702.

and Delp before the A.S.T.M.[13] The object of the experimental work was to put forward a method of recovering the asphalt from paving mixtures in as nearly the original state as possible. Asphalts from Mexican petroleum were dissolved in carbon bisulphide and the carbon bisulphide was then distilled off at 180 mm. vacuum, and it was found that the asphalts recovered were almost unchanged in essential physical properties. Artificial mixtures of the same asphalts of different penetrations and sand and limestone dust were made to correspond with a typical sheet-asphalt mixture. Carbon bisulphide was used to extract the asphalt, the solvent removed by partial vacuum distillation and physical properties of the recovered asphalt determined. It was found that owing to the heating necessary in mixing with sand and limestone the specific gravity, flash and fire points of the asphalt have been slightly increased. The penetration of the recovered asphalt was in every case lower than the original asphalt.

R. G. W. Eadie[14] describes a new method of determining softening points, and gives comparison of his method with the Kramer & Sarnow method (which he finds gives the least consistent results), the Ball and Ring method, and the ½ in. Cube method.

The use of asphalt impregnated concrete piles has been adopted in Los Angeles harbour as a method of preventing the marked deterioration which has hitherto occurred in concrete used in Pacific Coasts Ports.[15]

The first progress report of the American Petroleum Institute on bituminous coating materials as a means of protecting pipe-lines against soil corrosion has been issued by K. H. Logan and E. H. Berger.[16] Six asphaltic and three tar products were applied to pipe at the pipe factory. None of the coatings was satisfactory under all conditions, and it is suggested that a coating better than any of the dip-coatings under test is needed. It was found that wrapping the pipe with loosely woven fabric which can be impregnated with the coating gave better protection by holding the coating in place.

For the determination of tarry substances in oil products, N. Chernoshukov[17] uses 5 c.c. of sulphuric acid (sp. gr. 1·84), and 5 c.c. of oil in a 15 c.c. graduate and shakes for five minutes. Where the oil and acid do not rapidly separate he adds one to two drops of naphthenic acid and centrifuges for five minutes, when a clear separation is obtained.

[13] *Chem. Abs.*, 1927, **21**, 2972.
[14] *J. Soc. Chem. Ind.*, 1927, **46**, 109T.
[15] G. F. Nicholson, *Chem. Abs.*, 1927, **21**, 1529.
[16] *Chem. Abs.*, 1927, **21**, 1543.
[17] *Chem. Abs.*, 1927, **21**, 4057.

An interesting article by G. Baume on the physical chemistry of road construction was given in Bull. Soc. Chem. Belg., 1927, **36**, 469.

He points out that coal tar pitch changes from solid to liquid much more rapidly than native or petroleum asphalts, and also that asphalts withstand shocks without breaking more easily than coal tar pitches which are very brittle.

He discusses the production of bituminous emulsions, and gives the properties of a product "arcite," developed by his colleagues and himself. This material is a mixture of asphalt or pitch with a plastifying agent and an emulsifying agent, which emulsifies readily with water under certain conditions.

Special Products.*

By W. J. Wilson, F.I.C., A.C.G.I. (Member).

Paraffin Wax.—C. C. Buchler and G. D. Graves[1] obtained pure fractions of normal paraffins ranging between $C_{18}H_{38}$ and $C_{43}H_{88}$ from various paraffin waxes. Each fraction was found to crystallise normally in plates either from solution or by solidification from the liquid phase. The alternative formation of needle crystals from impure waxes appeared to be due to the influence of soft wax. These experimenters also made the interesting observation that on the recombination of paraffin distillates obtained under high vacuum with the residuum the mixture was identical with the original material, so further disproving the theory that the change from amorphous to crystalline paraffin is associated with chemical decomposition or reconstitution.

F. H. Rhodes, C. W. Mason and W. R. Sutton[2] fractionated "slack wax" by sweating, obtaining both needle and plate crystals, the relative proportions of which were determined by the conditions. It was shown that there is actually only one type of paraffin crystals, the needles consisting of curled or "rolled up" plates.

F. W. Sullivan, W. J. McGill and A. French[3] give valuable data on the heat of solution of paraffin, and the same authors[4] have studied the solubility of paraffin.

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* Paper received May 17th, 1928.

[1] *Ind. Eng. Chem.*, **19**, 718.
[2] *Ind. Eng. Chem.*, **19**, 935.
[3] *Ind. Eng. Chem.*, **19**, 1040.
[4] *Ind. Eng. Chem.*, **19**, 1042.

Oxidation Products.—W. Ledbury and E. W. Blair[5] publish the results of an extensive investigation of the production of formaldehyde by oxidation of methane, ethylene and hexane. The costs of the process on a large scale are estimated and proposed plants described. While the results obtained were good, the process is not at present commercially profitable.

S. S. Medvedev[6] also gives the results of the oxidation of methane to formaldehyde, a number of catalysts having been tried, of which lead borates and phosphates gave the best yields.

F. Francis and N. E. Wood[7] record the compositions of a number of acids and a ketone obtained by oxidation of paraffin.

M. Freund[8] obtained a mixture of oxidation products by passing gasoline vapour and air through a heated iron tube filled with petroleum coke.

A paper by G. T. Koch and G. A. Burrell[9] describes the production of amyl acetate from natural gasoline. An account of the researches leading up to this process is given and some cost figures are included.

S. D. Kirkpatrick[10] also describes the industrial production of amyl alcohols and amyl acetate from pentane. This interesting paper includes a survey of the economic factors.

C. P. Harris[11] gives an account of the production of isopropyl alcohol.

Bitler and James[12] describe the first commercial plant for the catalytic oxidation of hydrocarbons, in operation at Nyack, N.Y., U.S.A. The product "Aldehol," obtained by oxidation of Pennsylvania kerosine, is said to be used as a denaturant. The plant is stated to have a capacity for treating 4000 gallons of kerosine daily, and to be capable of handling gas oil and spindle oil also. The production of various ethers, alcohols, esters, aldehydes and ketones is anticipated.

Attention is drawn also to a number of patents on the production of alcohols and other oxidation products.

Insecticides.—E. R. de Ong[13] addressing the American Petroleum Institute, estimated that there is a potential use of 170,000—250,000 bbls. per annum of petroleum distillates in California alone for use for insecticidal purposes, and it is understood that

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[5] *Dept. Sci. Ind. Research Rept.* 1.
[6] *Trans. Karpov. Inst. Chem.*, **1924**, (3), 54.
[7] *J. Chem. Soc.*, **1927**, 1897.
[8] *Zeit. angew. Chem.*, **40**, 368.
[9] *Indv Eng. Chem.*, **19**, 442.
[10] *Chem. Met. Eng.*, **34**, 276.
[11] *Oil Gas J.*, **25**, (36), 138.
[12] *Trans. Amer. Inst. Chem. Eng.*
[13] *Oil Gas J.*, **26**, (41), 141.

this application of petroleum is increasing notably in many parts of the world.

J. J. Davis, W. W. Yothers, A. J. Ackerman and L. Haseman[14] summarise replies to a questionnaire addressed to entomologists working on insecticide oil problems. The effects of oil emulsions on insects and on plants and other subjects are dealt with.

E. L. Griffin, C. H. Richardson and R. C. Burdette[15] find that emulsions containing relatively large droplets of oil are decidedly more effective than those in which the droplets are smaller, probably because more oil is retained on the plant surface.

E. R. de Ong, H. Knight and J. C. Chamberlain[16] state that for citrus trees kerosine is safer than oils of higher boiling point, but is unsatisfactory as a scalecide. Highly refined lubricating oils are preferred for use in summer A high proportion of unsaturated hydrocarbons is liable to cause serious injury to trees. A quickly breaking emulsion is preferred.

E. L. Green[17] shows that an oil boiling between 240° and 300° at 40 mm. pressure possesses maximum toxicity. No relation is found between toxicity and either the viscosity or the type of crude.

Decolorising treatment increases the efficiency of the oil.

E. R. de Ong[18] discusses the effects of oils of different volatility, saturation and degree of emulsification, and the relation of other physical and chemical properties to insecticidal action.

I. G. Farbenindustrie A.-G.[19] propose the use of ammonium naphthenate or of halogenated naphthenic acids or their salts with or without the addition of hydrocarbons or their halogen derivatives as insecticides.

Miscellaneous.—The subject of naphthenic acids is dealt with in a monograph, " Chemie, Technologie und Analyse der Naphthensäuren " by M. Naphtali.

Y. Tanaka and T. Kuwata[20] in continuation of earlier work, separated some pure naphthenic acids and determined their physical properties.

The production, composition, properties and application of petroleum sulphonic acids is dealt with by G. S. Petrov, S. I.

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[14] *J. Econ. Entomol.*, **20**, 229.
[15] *J. Agric. Research*, **34**, 727.
[16] *Hilgardia*, **2**, 351.
[17] *Ind. Eng. Chem.*, **19**, 931.
[18] *J. Econ. Entomol.*, **19**, 733.
[19] *Ger. Pats.*, 433,653, and 435,389.
[20] *J. Soc. Chem. Ind.* (*Japan*), **30**, 48.

Dimakov and F. T. Taksa.[21] Tilitschejev and Dumskaja[22] also publish a paper on the production of these substances.

Some attention has been given to the use of petroleum oils for the preservation of wood. L. P. Curtin and M. T. Bogert[23] find that heavy petroleum is superior to creosote as a waterproofing oil, and is more permanent in its effect. The former is, however, non-poisonous to dry rot. A suitable highly toxic substance should be added to the oil. A. M. Howald[24] publishes results showing the relative penetrative powers of different types of oils applied to wood.

[21] *Seifen. Zeit.*, **54**, 163, 182, 204, 221, 241, 261, 284.
[22] *Neftj. Khoz.*, **11**, 738.
[23] *Ind. Eng. Chem.*, **19**, 1231.
[24] *Chem. Met. Eng.*, **34**, 353, 413.

Analyses and Testing of Petroleum Products.*

By J. S. JACKSON, B.Sc., A.I.C. (Member).

THE methods for testing Petroleum Products having reached a reasonably stable condition as the result of the efforts of various standardising bodies, the amount of development and progress to be reported is naturally not very great. The ever increasing demands of specifications and the rapid growth of highly specialised applications of petroleum products are, however, constantly emphasising the necessity for more accurate and more discriminating tests.

In the case of gasoline it has become increasingly evident that those chemical tests which can be readily and accurately made do not discriminate reliably between or evaluate truly the various types of spirit, and the general trend has been towards engine tests in some type of variable compression engine. Parallel with this movement endeavours have been made to develop spontaneous ignition tests and equilibrium distillation methods which will give results in line with those obtained in engines. Thus, Weerman and Egerton and Gates have published much interesting work upon the determination and significance of igniting temperatures.[1]

As might be expected in view of commercial considerations, there is nothing very special to record in connection with the testing of kerosine, but many items of interest in connection with the testing of kerosine were dealt with in a paper upon "The Burning of Mineral Oils in Wick Fed Lamps."[2] In this paper a simple

* Paper received June 6th, 1928.
[1] *J. Inst. Petr. Techn.*, 1927, **13** (61).
[2] *J. Inst. Petr. Techn.*, 1927, **13** (62).

method of comparing the burning properties of kerosines was described. By this method kerosines are evaluated according to their "Tendency to Smoke." Attention was also directed to the important influence of the viscosity of a kerosine upon its burning properties.

Attention is very forcibly directed towards lubricating oil by the numerous and persistent efforts to evolve tests which will assist the user in choosing oils well suited for his special purposes. Thus, we find many workers striving to evolve coking tests, oxidation tests, corrosion tests, etc. From all this volume of work the Ramsbottom coking test has emerged in a carefully standardised condition, and the Air Ministry have developed an oxidation test which attains a fair degree of accuracy. The relation of such tests to actual practice cannot, however, be regarded as established.

Turbine oils have attracted special attention, and the user has now available an almost bewildering array of demulsification tests by means of which he may gain information of rather doubtful value as to the behaviour of the oils in which he is interested. Among the more widely used demulsification tests recently developed we find the A.S.T.M. test for Steam Emulsion of Lubricating Oils, D. 157-27, the Conradson method (A.S.T.M., 1916) and the Admiralty method. The last mentioned, a severe test involving emulsification with water and circulation by means of a rotary pump, is capable of a very satisfactory standard of repeatability.

Much interesting work has also been done upon various tests designed to give some indication of the stability of turbine oils in actual use. Rogers and Miller have described a stability test[3], which consists in passing excess of moist oxygen through a quantity of the oil containing a known amount of iron wire at 100° C. Periodical samples are withdrawn and the Herschel demulsibility, acidity and rate of sludge formation determined. It is claimed that this test indicates with reasonable accuracy the behaviour of the oil in a "dry" turbine.

In connection with the testing of lubricating oils for general purposes the Bureau of Standards have published a description of an apparatus for determining the efficiency of gear oils. The apparatus consists of two gear boxes with a train of gears in each so arranged that the load on the teeth can be altered by means of a torsion device.

A corrosion test which had been employed in connection with the examination of used lubricating oils from Diesel engines was described by Young.[4]

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[3] *Ind. Eng. Chem.*, Feb., 1927.
[4] *J. Inst. Petr. Techn.*, 1927, **13** (65).

Among the many developments in general methods of testing the following are probably of sufficient interest to merit description.

An economical method of chemical interest has been described by Marcussen[5] for the determination of the asphaltum content of mineral oils. In this method the asphaltum is precipitated by means of a 5 per cent. ethereal solution of ferric chloride.

The Waters method for determining sulphur[6] consists essentially of direct oxidation with concentrated nitric acid saturated with bromine. The method has the outstanding merit that it requires no special apparatus and many samples can be tested at once. In the hands of a careful operator the method is more convenient than the more usual bomb method.

Very definite improvements have been effected in the Lovibond Colorimeter, which is now provided with a special lamp and "daylight" reflector. The colour standards are now mounted in a convenient magazine.

A particularly interesting method for the determination of the oil in paraffin wax was described by Diggs and Bucklers.[7] The method makes use of the refractometer, the percentage of wax present being determined by a consideration of the refractive indices of the sample before and after filtration through highly absorbent clay by which the oil is retained.

During 1927 the American Society for testing materials have been able to publish many hitherto tentative methods in a final standard form, while the Sligh oxidation test is put forward as a proposed method.

A proposed method for the estimation of oil in refined wax has been worked out by Wilson and Wilkin. In this method a residue containing the whole of the oil and some wax is obtained by the proper use of ethylene dichloride as a solvent. The amount of wax present in such a residue, and hence the amount of oil in the original wax, can be determined by observing the effect of known quantities of the residue upon the solidification point of a specially chosen paraffin oil. This involves the use of a calibration curve which relates the rise in solidification point of the paraffin oil to known additions of wax.

Full particulars of the progress made by the A.S.T.M. may be found in the Report of Committee D. 2 of the American Society for Testing Materials.

Much work remains still to be done before it can be claimed that adequate testing methods are available, but the progress made and the degree of standardisation achieved may be viewed

[5] *Chem. Ztg.*, 1927, **51**, 190.
[6] *Refiner*, Oct., 1927.
[7] *Ind. Eng. Chem.*, 1927, **19**.

with some measure of satisfaction. In spite of the success achieved, however, there still remains a great deal of uncertainty as to the correct interpretation of the results obtained in terms of actual practice, and in this direction there remains much scope for the chemist's ingenuity.

Synthetic Fuels.*

By Alfred W. Nash, M.Sc., F.C.S., M.I.Mech.E. (Member) and Arthur R. Bowen, M.Sc., Ph.D., F.I.C. (Associate Member).

The preceding year has been characterised by the granting of a large number of patents of an important nature, apart from the publication of several valuable experimental papers and reviews. For the former the I.G. Farbenindustrie Aktiengesellschaft are responsible for no small share, and the attitude and opinion of this concern have been stated by Krauch, whose observations on the technical side of the process are of special interest. The situation of petroleum substitutes during last year is well expressed by Dunstan and Shatwell[1], who point out that the present is a singularly inopportune time to discuss the question of synthetic fuel owing to the over-production of petroleum, yet political and strategic purposes constitute the driving force of its investigation.

Reviews upon the subject of the possibilities of synthetic fuels and discussions of their relative importance are put forward by Nathan[2], Nash[3], Dunstan and Shatwell (*loc. cit.*), King[17] and Florentin.[4]

For classification purposes the progress of the work on synthetic fuel can be divided under four sections :—

1. Berginisation : (*a*) Non-catalytic ; (*b*) Catalytic.
2. Carbon monoxide reduction.
3. Conversion of methane and natural gas to higher hydrocarbons.
4. Other methods.

1. *Berginisation.*—In view of recent developments the work of this field may now be sub-divided into the further sections : (*a*) non-catalytic, and (*b*) catalytic.

(*a*) The berginisation of squalene was found by Ormandy, Craven, Heilbron and Channon[5], to yield an oil of which all the

* Paper received March 3rd, 1928.

[1] *Institute of Fuel*, Nov. 24th, 1927.
[2] *J. Soc. Chem. Ind.*, 1927, **46**, 213T.
[3] *J. Inst. Petr. Techn.*, 1927, **13**, 681.
[4] *Bulletin Soc. Chim. Industrielle*, 1927.
[5] *J. Inst. Petr. Techn.*, 1927, **13**, 1.

fractions were similar to natural petroleum. Pinene was also investigated, and found to behave in a similar manner to the fish liver oil. Waterman and Perquin have submitted paraffin wax to treatment at 450° C. with and without hydrogen, and have shown the difference between the hydrogenated and cracked products, including a study of the hexane, heptane and octane contents of the spirits.[6] The berginised spirits are more saturated and stable in character than those from the cracking experiments. A further contribution to our knowledge of berginisation, consisting of a technical chemical investigation of hydrocarbon mixtures, was made by the same authors[7]; in this work the physical and unsaturated properties of several samples of hydrocarbons were studied. The method of investigation was applied to the products obtained by cracking paraffin wax in the vapour phase, this process being carried out in a vacuum. Notwithstanding the high temperature used (450-460° C. for 4 hours) no cracking occurred, the reason being that the time in the cracking spiral was only 4 seconds. Cracking paraffin wax with 10-12 per cent. of aluminium chloride at 250-260° C. for 1-4 hours resulted in a residue of 56 per cent. of unchanged wax and the formation of 25-30 per cent. gasoline. (*b*) In the field of catalytic hydrogenation of coal and other bituminous substances a large number of patents have appeared from the I.G. during the past year. Krauch, a director of this concern[8], discusses the technical and economic aspects of the better utilisation of coal with special reference to the two connected high pressure processes: the liquefaction of coal and the fixation of atmospheric nitrogen. He discusses the economic production of hydrogen, and mention is made of the modern method of the I.G. of passing a mixture of water gas and producer gas with steam over a catalyst, followed by the removal of carbon dioxide. The Winkler process for the production of water gas from granular brown coal is explained. A review is made of the earlier work on the liquefaction of coal in Germany, and the view of the I.G. is given—namely, that they are not of the opinion that the atmospheric pressure work of Fischer is preferable to the pressure methods. The I.G. claim similar results in their pressure work to those of Fischer with the additional advantage of greater condensation and capacity facilities. They also think that the hydrogenation of coal is the most promising of the two processes for its liquefaction. In his treatment of coal, Bergius was dependent entirely on the nature of the coal as regards the character of the product obtained by hydrogenation.

[6] *Bulletin Soc. Chim. Industrielle*, 1927; *Rec. Trav. Chim. Pays Bas*, 1927, **46**, 813.
[7] *J. Inst. Petr. Techn.*, 1927, **13**, 413.
[8] *Stahl und Eisen*, 1927, **47**, 1118.

Krauch, explaining that a process becomes more valuable as the products are improved, shows that the object of much research has been directed towards the formation of light aromatic and aliphatic hydrocarbons. Coal is heated until the molecule is "cracked," and the molecule fragments, which are unstable, tend to give up hydrogen and also polymerise to more stable substances. These fragments hydrogenate under high hydrogen pressure. The process of hydrogenation is influenced by temperature, pressure, velocity of hydrogen and steam, and, *above all, by different catalysts.* By the use of catalysts it can be arranged that the chief products are light, simple hydrocarbons, and also that there is formed a more or less large yield of these of aromatic nature. Great technical difficulties are to be met with in the commercial application of this process—*e.g.*, in the introduction of solid substances during the reaction into the high pressure furnaces, and their subsequent extraction. Difficulties also arise on account of the high sulphur content of the crude material. They intend to make, at the Leuna works, from brown coal, gasoline and valuable oils, especially lubricants. The economics of the production, transport and selling of the German synthetic fuels are discussed in the *Economist.*[9] The I.G. have been licensed to transport synthetic oil or petrol at the cheaper "D" rate instead of the more expensive "C" rate by the German Railway Company. An approximate estimate of profits of the coal liquefaction business has been put forward by Bruckmann (of the Erdol u. Kohlverwertung A.-G.), and in a recent report of the German banking firm, Schwarz Goldschmidt & Co., a list is given of the direct and indirect connections of the I.G. with many foreign chemical and petroleum firms.

The I.G. patents of last year, twenty in number, cover the manufacture of liquid and other hydrocarbons and derivatives, from coal and similar materials; thus the characteristic feature of E.P. 247,582 is the hydrogenation of bituminous materials at 50 atm. (or over) pressure, and using combined nitrogen (ammonia or ammonium sulphide) as a catalyst. Only small amounts of phenols are obtained, and under specified conditions yields of 80 per cent. liquid products are quoted. E.P. 247,583 refers to a similar process, where catalysts containing molybdenum or its compounds are used—*e.g.*, molybdenum sulphide, molybdic acid or ammonium molybdate. Molybdenum catalysts are claimed to be remarkably immune from catalyst poisons and examples using brown coal are stated. Combined sulphur (E.P. 247,584) is also claimed as a catalyst in the form of one or several sulphides. The sulphides of metals of the iron group are specially mentioned.

[9] 1927, **105**, 927, 1083.

An additional series covers similar conditions applied to the products of distillation or extraction of coal and allied substances. Thus E.P. 247,585 quotes pressed precipitated cobalt sulphide for the hydrogenation of crude cresylic acid at 150 atm., and at 400-500° C., when *considerable reduction of phenols to hydrocarbons* is claimed. In E.P. 247,586 molybdenum catalysts are applied in the treatment of distillates, etc., and a thin, nearly colourless product of sp.g. 0·83 consisting of hydrocarbons free from phenols, coke and asphalt, with only a small quantity of gaseous products, is claimed by treatment of brown coal producer tar. In E.P. 247,587 combined nitrogen is again the catalyst, but also applied to distillates. The patent E.P. 249,155 relates to improvements in plant construction in hydrogenation where gas mixtures containing hydrogen and carbon oxides are used under pressure at elevated temperatures. Special metals and alloys are recommended for the hot parts of the tube. E.P. 249,156 covers the conversion of coal into benzines and lubricating oils by the action of hydrogen at elevated temperature and under pressure, *followed by a second stage where different catalysts may be necessary*. Besides the catalysts covered in earlier patents, such methanol catalysts as zinc oxide are mentioned. E.P. 249,493 extends the use of combined sulphur catalysts to the other bitumens or distillates—*e.g.*, shale-oil, ozokerite, crude oil and asphalt. The extension of these processes to mineral oil or other bitumens is covered by E.P. 249,501, where valuable hydrocarbons are claimed from nearly solid crude oil residues by hydrogenation with molybdenum catalysts. From such a starting material a nearly colourless, mobile, completely saturated oil of which 90 per cent. is colourless benzine boiling below 150°, is claimed. Jura shale-oil and Mexican asphalt yield similar benzines. In E.P. 250,948 combined nitrogen is used in the treatment of mineral oils and bitumens, and in E.P. 251,264 tungsten or chromium catalysts are specified in the hydrogenation of coal tars and mineral oils. E.P. 253,911 is more purely chemical, and describes the conversion of certain secondary aromatic or mixed aliphatic-aromatic alcohols into cyclic hydrocarbons, by the passage of the vapours over active charcoal. The gases capable of use in these processes are described in E.P. 254,713, where hydrocarbon vapours are decomposed with air or oxygen in the presence of catalysts to form the requisite hydrogen (see Section 3). Minor points in the preparation of catalyst absorbents and purification of hydrocarbons are covered in E.P.s. 255,904 and 255,905. The use of catalysts—*e.g.*, sulphides of heavy metals in catalytic dehydrogenation such as isobutyl alcohol to isobutyraldehyde—is covered in E.P. 262,120. An improvement in the arrangement in coal hydrogenation is claimed in E.P. 272,829, where the vapours only pass

over certain catalysts. Cracked products and acid sludge are mentioned in the additional patent E.P. 274,401, where molybdenum catalysts are again specified for bitumen hydrogenation, and in E.P. 274,404 tar vapours are passed from the first to the second stage of the process without intermediate condensation. E.P. 277,273 is a further improvement on the metal used—viz., copper, silver, aluminium, chromium, manganese or special steels, etc., in the hot and cold regions of the high pressure apparatus, and all parts of the plant are resistant to the action of carbon monoxide.

Along with this large number of catalytic hydrogenation processes covered by the German concern we have two patents relating to the important work of Florentin and his co-workers. Kling and Florentin E.P. 253,507 describe a process for obtaining light hydrocarbons from heavy cyclic hydrocarbons or derivatives. Light saturated hydrocarbons are claimed from such materials by treatment with hydrogen at an initial pressure of at least 50 kg. cm.^{2} and at 350-460° C., and with non-hydrogenating catalysts. The latter may be chlorides of other halides of alkaline earths, or earth metals, or chlorinating or other halogenating agents. Naphthalene, heavy tars, oils, pitch, colophony and coke are described as amenable to the process. Florentin, Kling and Matignon E.P. 263,082, describe a further process to produce light hydrocarbons from oxygenated organic compounds in the continuous liquid phase at 350-480° with hydrogen under pressure, in the presence of dehydrating catalysts—*e.g.*, thoria. With Autun shale-oil, saturated hydrocarbons were formed, and a product obtained of which 48 per cent. distilled below 205° C.

2. *Production of Liquid Fuels from Carbon Monoxide and Hydrogen.*—During this last year the patent of Fischer and Tropsch covering the production of paraffin hydrocarbons with more than one carbon atom, has appeared (E.P. 255,812). The conditions claimed are that oxides of carbon and hydrogen are passed over methane forming catalysts at atmospheric pressure and at temperatures of 80-100° C. below that at which methane is the main product. Nickel is excluded as a suitable catalyst, and a mixture of zinc oxide and finely divided iron is quoted as a typical case. In a later communication[10] these investigators describe the preparations of a solid hydrocarbon which appears to have the composition $C_{70}H_{142}$, from the reduction of carbon monoxide with hydrogen under 10-15 atm. pressure and in the presence of a catalyst consisting of 4 parts iron, 1 part copper and ½ per cent. of potassium carbonate held at 280° C. This hydrocarbon is described as a

[10] *Ber.*, 1927, **60**, 1330.

white starchy mass, melting at 90-180° C., and with a molecular weight of 1000.

In connection with Fischer's catalysts the work of Meyer and Scheffer[11], on the formation of carbides in the systems metal-carbon-hydrogen and metal-carbon-oxygen, is of interest.

An important series of experiments describing the experimental conditions, and products obtained, in the catalytic reduction of carbon monoxide with hydrogen is put forward by Elvins.[12] The production, not only of saturated aliphatic hydrocarbons, but also olefinic and water soluble oxygenated compounds, is described, and details are also given of catalyst preparation. The choice and preparation of the catalyst is made the object of study of the earlier experiments, and comparing the yields of products in the case of precipitated oxide and catalysts prepared by the fusion and decomposition of nitrates, the latter were found to give the greatest conversion. Later, fused oxides were found to provide a time economy in the preparation of catalysts and also a hard stable granule. The liquid and gaseous products of reaction are described, and included in the latter are the gaseous olefines, which were scrubbed from the exit gases by means of sulphuric acid.

A series of experiments on the catalytic preparation of unsaturated hydrocarbons from carbon monoxide and hydrogen is described by Hoover, Dorcas, Langley and Mickleson.[13]

For a theoretical paper dealing with the equilibrium conditions in the formation of hydrocarbons and alcohols from water gas the communication of Smith should be studied.[14] The free energy of formation of methane, ethane, propane and benzene, and also of methyl, ethyl and *n*-propyl alcohols are calculated. The value for the increase in energy brought about in the formation of these substances from carbon monoxide and hydrogen is obtained from these free energies and also from those of the oxides of carbon. From these equations the free energy increases in each case, $\triangle F$, accompanying the formation of these compounds from water gas at any temperature T, is given by the usual equation $\triangle F = -RT \log_e K$. The values of K at 25°, 300° and 400° C. for the substances mentioned have been calculated on these lines. The values of K at all temperatures increase as the homologous series is ascended. It is deduced that given suitable catalysts it would be possible to produce any of the paraffin hydrocarbons from water gas at atmospheric pressure and at 300° C. *Benzene has a strong tendency to form at these temperatures* and a catalyst

[11] *Rec. Trav. Chim.*, 1927, **46**, 359.
[12] *J. Soc. Chem. Ind.*, 1927, **46**, 473.
[13] *J. Am. C. S.*, 1927, **49**, 796.
[14] *Ind. Eng. Chem.*, 1927, **19**, 801.

should be found for its formation. From the thermodynamic standpoint the ease of formation depends *directly on the pressure* and inversely on the temperature. From the values of K obtained the maximum possible yields of any product under a definite set of conditions can be calculated.

A number of additional patents on the manufacture of methanol, higher alcohols, and other oxygenated compounds have appeared also, and it seems now that the pressure catalytic reaction of carbon monoxide and hydrogen has definitely entered the field of pure synthetic organic chemistry. Among these the following may be quoted: Audibert E.P. 271,538 (methyl alcohol), I.G.G.P. 411,272 (higher aliphatic acids), Patart, E.P[s]. 249,519 (production of liquid hydrocarbons from heavy organic materials), 250,563 (synthesising and separating higher alcohols), 252,361 (regenerating contact masses), Casale, E.P. 252,713 (alcohols and oxygenated organic compounds). The use of butyl fermentation gases has been shown to be a source of methanol forming gases by Woodruff.[15]

3. *Synthetic Spirits, etc., from Methane and Gaseous Hydrocarbons.*—Various processes have been patented in which methane and its homologues can be converted into liquid products either directly or indirectly, but experimental work in this field is somewhat scanty. Among the latter the conversion of methane, natural gas, etc., into carbon monoxide and hydrogen is covered by the B.A.S.F. (E.P. 266,410), in which partial oxidation to the required mixture in the presence of catalysts is claimed. The decomposition of gaseous hydrocarbons with water vapour at high temperature is covered by the I.G. (E.P. 265,989). Casale (E.P. 274,610) also describes the preparation of carbon monoxide and hydrogen mixtures by decomposition of methane and steam at temperatures above 1000° C., below atmospheric pressure and in the presence of catalysts. Such indirect processes thus lead to a gas mixture suitable for further treatments as are discussed under Section 2.

Three methods are covered by patents in which methane is directly converted into hydrocarbons of higher carbon content. Thus Le Petrole Synthetique Soc. Anon. and Folliet (E.P. 271,767) claim such a process, in which methane is subjected to a gradual heating, followed by a sudden cooling when the highest temperature is reached. The ethylenic hydrocarbon output is increased with a higher vacuum during cooling. Spindler and Goudet E.P. 255,493 apply a three staged process, namely: (*a*) methane is heated to 500-950° C.; (*b*) it is cooled to maintain the conditions of dissociation, and (*c*) it is subjected to the action of a catalyst. Zinc chloride, active charcoal, aluminium and magnesium powders are among

[15] *Ind. Eng. Chem.*, 1927, **19**, 1147.

those specially mentioned. Pressures of 70-250 atmospheres are also recommended.

The semi-commercial scale gas pyrolysis plant of the Anglo-Persian Oil Co. is mentioned by Williamson (" In a Persian Oilfield," p. 70), in which benzene among other substances is produced from stripped low-pressure gas.

4. *Other Methods.*—Otto[16] suggests the uses of boron fluoride as a polymerising agent in the production of oils from ethylene and its homologues, and compares the synthetic oils with the best American lubricating oils.

A process for the production of benzene from phenolic vapours and a reducing gas is claimed by Irinyi (E.P. 273,493), in which the temperature of reaction 750° C is quoted, when phenol and hydrogen react to form benzene.

CONCLUSION.

A survey of the claims of the previous year indicate many new results, some of which, up to the present, have not been substantiated by published experimental work. The catalytic hydrogenation of coal at high hydrogen pressure appears to be an important advance, and the pronounced effect of catalysts in this reaction has been shown by the authors in the past. The claims in the pyrolysis of methane are undoubtedly the most difficult to correlate with our present knowledge of the thermal decomposition of that gas which has the greatest tendency to break down into its elements only, although its immediate homologues ethane, propane and butane, are known to form higher aromatic hydrocarbons at moderately high temperatures.

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[16] *Brenn. Chem.* 1927, **8**, 20.
[17] *J.Soc. Chem. Ind.*, 1927, **46**, 181T.

Oil Engines.*

By J. F. ALCOCK, B.A.

THE year, though perhaps uneventful, has seen a steady progress in all classes of work. At present the main field for the oil engine is in marine work, for propulsion and auxiliary services, and its position is now firmly established for all classes of mercantile vessel, other than the very largest liners. For warships, other than submarines, steam still holds its own, the enormous power

* Paper received May 4th, 1928.

required, and the severe limitations of weight and space, putting the orthodox Diesel installation entirely out of court.

Compared with 1926, the total horse-power installed for ship propulsion increased by about 15 per cent, and at the end of the year the total on order slightly exceeded the steam horse-power.

A very significant feature is the firm adherence to the Diesel ship shown by owners having experience of both classes of vessels. A table published in *The Motor Ship* gives particulars of 28 owners, with oil-engine experience dating back, in some cases, to 1912, who between them operate no less than 279 motor-ships, and only 33 steamships, other than those they had before taking delivery of their first motor-ship in each case. In other words, an owner who has once had a motor-ship very rarely goes back to steam.

This is a very important point, since the adherents of steam are very prone to set off, as against the demonstrably lower fuel and labour charges of the Diesel, alleged shortcomings in less commensurable factors such as reliability and depreciation. The most useful evidence on such points is the action of such shipowners as have had experience of both types, and this, as we have seen, is decisively in favour of the motor-ship.

Without doubt, the chief feature of the year is the rapidly increasing popularity of the large oil-engined passenger liner. Experience gained with pioneer vessels such as the *Gripsholm* and *Aorangi* has been extremely satisfactory, and, as with cargo vessels, the verdict of lines having a mixed fleet is emphatically in favour of the Diesel.

The following particulars quoted from *The Motor Ship* of twelve liners owning Diesel passenger vessels speak for themselves :—

Diesel liners in service	22
Do do on order	18
Steam liners ordered since delivery of first motor-ship	2

The largest motor-vessel completed this year was the *Augustus*, of 33,000 tons, driven at 21 knots by four M.A.N.-Savoia double-acting two-stroke engines each of 6250 b.h.-p. Next in order is the *Saturnia*, also Italian, of 23,500 tons and 21 knots speed. Hers are the largest marine oil engines in service, each of the two installed developing 10,000 s.h.-p. at 125 r.p.m. They are eight-cylinder, double-acting, four-cycle engines made by Burmeister and Wain.

An interesting point about this installation is the use of supercharge, a heroic step with cylinders of this size.

As regards single-acting plant, the largest installations are in the *Bermuda*, with her four 2900 b.h.-p. Doxford engines, and the *Christiaan Huyghens* with two Sulzer engines of 5,800 b.h.-p.

There now seems to be little doubt that the thermal and mechanical problems arising in these large engines have been satisfactorily dealt with, and proposals are on foot for installations up to 100,000 b.h.-p. on four shafts. This would easily cover all commercial requirements.

A significant point about recent installations is the enormous auxiliary power required. In order to get the highest possible output at the propellors, all auxiliary services are taken off the main engines and driven independently, and since on most of these services depends the reliability of the main engines, extensive duplication is necessary. Thus the *Saturnia*, with 20,000 b.h.-p. on the main engines, has an auxiliary power installation of no less than 8300 b.h.-p., 4950 b.h.-p. to drive compressors for injection and manœuvring air, and 3350 b.h.-p. generating electricity to drive the supercharge blowers and for miscellaneous services. Again, in the *Augustus* the auxiliary engine room actually takes up more floor space than does the main engine room.

These and similar instances appear to indicate that a general cleaning up of the auxiliary problem is about due. The use of airless injection, now spreading to double-acting engines, is a favourable sign, as eliminating the blast-air demand, but the manœuvring problem remains. As regards electricity supply, the heaviest demand, where the compressors are driven direct from the main or from auxiliary engines, is for the operation of high-speed supercharge and scavenge blowers, and in this connexion the use of steam turbo-blowers, supplied with steam from exhaust-heated boilers seems worthy of investigation.

An innovation is the installation of Diesel engines for use at cruising speeds, in two light cruisers, H.M.S. *Adventure*, and the German *Karlsruhe*. For full speed steam is still employed, since oil engines cannot yet be made to give the very high outputs required within the permissible limits of weight and space.

Other interesting installations are those in the *Monte Cervantes* and *Eurybates*. The former is driven by four 1500 b.h.-p. M.A.N. engines running at 210 r.p.m. geared to two propellor shafts running at 75 r.p.m. This is the third installation of this type for the same owners, so it may be assumed that they have proved satisfactory in service. As there is a distinct saving in weight, bulk and cost over direct coupled engines, one may expect an increasing use of this type of plant.

The *Eurybates* is fitted with a new form of Scott-Still engine. Steam is raised, as in earlier Still engines, by the waste heat in the cylinder jackets and exhaust, but it is utilised not, as before, in the underside of the combustion cylinders, but in separate steam

cylinders of orthodox type, whence it passes to a turbo-blower which supplies scavenge air to the combustion cylinders.

In land work increasing interest is being shown, especially in Germany, in the use of oil engines to take peak loads in electric power stations, their especial advantage as compared with steam plant lying in the absence of stand-by losses.

A 15,000 b.h.-p. M.A.N. double-acting engine was installed for this purpose last year at Hamburg, and has proved so satisfactory that two further engines, each of 12,000 b.h.-p. are now installed for the same purpose at Berlin. These engines run at 215 r.p.m., a high speed for this size, and have airless injection. This high speed has the advantage of reducing the capital cost per b.h.-p., an important point for peak load work, since the interest, etc., charges form a financial "stand-by" loss of serious proportions.

For their power these engines are very compact, weighing only 55 lb per b.h.-p.

An extremely interesting engine is the 1750 b.h.-p. Fraser and Chalmers unit supplied for electricity generation in London. The design of this engine, which runs at 300 r.p.m., shows clearly the influence of modern high-speed practice, the pistons, of 21·5-inch bore, being of aluminium alloy and the cylinder liners of case-hardened steel.

This construction should greatly reduce wear on the cylinder liners, a problem which has recently been receiving a good deal of attention.

High-speed Engines.

Information as to these is somewhat scanty. New engines are produced, but as yet there is hardly sufficient time for their behaviour in actual service to be assessed. In Germany they are still being developed mainly for lorry driving, two notable newcomers being the Mercedes-Benz and the Junkers, the latter being a very neat opposed piston two-stroke. In America a number of small high-speed marine engines, running at 600–800 r.p.m., have been produced.

There now seems little doubt that the small high-speed Diesel can, if well designed, give a performance at least equal to that of slow-speed engines, at speeds up to 1200–1500 r.p.m. and possibly higher. The chief obstacles to their more extended use is really the present low cost of petrol, which reduces the saving due to the oil engine to a figure which hardly justifies the greater initial cost and difficulty in operation.

On these grounds it seems hardly likely that the Diesel will, under present conditions, become popular for road transport, more

especially as the substitution of oil engines for petrol on any appreciable scale would tend still further to level out the price difference.

In marine work, however, the case is quite different, since on board ship the fire risk renders petrol a most undesirable fuel. Again, in this case the fuel bill is more important, the average power output being higher than in road work, and the duty more continuous. At present the small yacht, fishing boat, etc., has to choose between the petrol engine and its dangers, and the safer but more objectionable kerosine engine. A reasonably cheap and easily handled Diesel, in powers from 30–150 b.h.-p., should find in this service a ready market.

Of the aircraft Diesel there is as yet no definite sign, though in this case its welcome would be very cordial. Apart from the saving on the fuel bill, which is serious owing to the necessity for high-grade spirit, the reduction of fire risk would be an enormous asset, for this risk is at present, very naturally, a most powerful deterrent to air travel.

The difficulty in designing an aircraft Diesel is the fact that the power output from a given cylinder is appreciably less than that of the petrol engine, while the construction must be heavier, owing to the greater cylinder pressures. Both these factors increase the ratio of weight to h.-p. at present to a prohibitive extent, in spite of the saving in fuel weight. In the absence of any new development giving a substantial increase in the ratio of mean to maximum pressure, success seems most likely to come by the use of naturally light designs such as the radial, or possibly by the development of a high-speed two-stroke, a cycle which is not suitable for petrol engines of any appreciable size.

Fuel Injection.

The airless injection system is slowly but surely gaining ground, and is gradually winning over the adherents of the older method. It has this year been successfully applied to double-acting engines, in which injection is always a difficult problem, owing to the design of the combustion chamber being complicated by the presence of the piston-rod.

An increasingly popular system is that common in "cold-starting" engines, where the combustion chamber is separated from the cylinder proper by a more or less restricted neck, the turbulence due to the forcing of the charge through this neck during compression being relied on to effect mingling of the fuel and air. This system allows of efficient combustion with single-orifice fuel injectors, a considerable advantage with small engines, in which the individual orifices of a multi-jet injector become so small as to give continued trouble with choking.

An interesting new-comer of this type is the "Acro" engine. In this the combustion chamber is contained in the piston and not in the cylinder head, which is thus left clear for valves.

Air injection shows little change, except that separately driven blast-air compressors are becoming increasingly common.

Two-stage injection, or the pre-combustion system, makes little headway. As a rule the fuel consumption is higher than with other systems, owing to greater heat losses, and it is very difficult so to regulate the rate of combustion as to insure smooth running.

Supercharging.

This is progressing rather more slowly than might be expected, though its adoption for the 10,000 b.h.-p. engines of the *Saturnia* shows that it has powerful adherents. It seems probable that this is largely due to the cost of the auxiliary engines and electric drive to the blowers, and perhaps to some doubt as to the behaviour of the high-speed blower motors in the hands of the ordinary engine-room staff. It is significant that the greatest progress has been made with the Büchi exhaust turbo-supercharging system, which eliminates the electric transmission, and should therefore effect a marked saving in cost. This system uses a really high degree of supercharge, usually 50 per cent., as against the usual 10–15 per cent. with the electric system. Here again the limitation in the latter case is probably due to the question of cost, since blowers for a 50 per cent. supercharge need a good deal of power.

During the year the Büchi system has been tested in service in small vessels. Details of its performance are not available, but from the fact that no less than fourteen seagoing installations are on order, one may assume that the existing units have proved a success.

Semi-Diesel Engines.

The true hot-bulb engine is now almost extinct, though in a few cases a small "hot spot" is retained to assist ignition, and electric heaters or starting cartridges to aid in starting.

The type survives mainly in yachts and other small vessels, and with the further development of the small Diesel seems likely to disappear.

Engine Knock and Anti-Knock.*

By A. Egerton, F.R.S.

(*a*) Engine Knock.

The subject of this review is opened by two important series of papers; first those of Ricardo[1] on the detonating properties of various fuels, and then those of Midgley and Boyd[2] on the "anti-knock" value of various substances, the most important of these "dopes" being lead tetraethyl.[3]

The words "detonation," "pinking" and "knocking" are all employed to designate the same phenomenon connected with the running of an internal-combustion engine on certain fuels. Ricardo points out (l. c.) the distinction between "pre-ignition" (auto-ignition prior to spark ignition) and "detonation," which is an abnormal type of combustion, setting in after the spark has already initiated combustion. A mixture prone to "pre-ignite" is not necessarily likely to "detonate" and *vice versâ*. Tizard[4] showed that tendency to detonate would depend not only on the ignition temperature but on the temperature co-efficient of reaction, and cites the cases of carbon bisulphide of heptane, of benzene and of hydrogen. The paraffin hydrocarbons detonate in accordance with their adiabatically determined ignition temperatures, because their temperature co-efficients are practically the same throughout. Detonation occurs towards the end of the passage of flame through the combustible mixture in the compression space, as shown by Ricardo[5] using quartz windows fitted in a cylinder head.

The use of the word "detonation" is perhaps somewhat misleading in view of the facts (1) that a "detonation wave" appears not to be propagated in mixtures of composition such as are used in the internal-combustion engine;[6] (2) that substances behaving as anti-knocks do not appreciably render the position of detonation later or delay the speed of detonation waves in hydrogen mixtures[8] or in acetylene or pentane mixtures,[7] even at high pressure and temperatures up to 230° C.

For combustion of a detonative type to be transmitted in a gaseous mixture the velocity of reaction has to be maintained sufficiently great to propagate the compression wave and combustion simultaneously; the layer immediately ahead of the advancing flame is ignited by compression and in some manner sufficiently activated to react with great rapidity. Wendlandt[10] has determined the strength of mixtures of CO/O_2 and of H_2/air capable of

* Paper received August 8th, 1928.

transmitting the detonation wave, and from these results and those of Egerton and Gates (l. c.) it seems unlikely that such a type of combustion could be set up in the short space of an engine cylinder head and transmitted through the charge, but actual experiments in bombs are not possible at temperatures corresponding to that of the charge in an engine.

The effect of increase in initial temperature is to decrease the tendency to set up detonation in a tube.[7,9] The effect of initial pressure is to render detonation earlier up to a certain limit.[7,9] A tendency to start a detonative type of combustion may occur at an irregularity or be set up by a dust particle in the tube, but a detonation wave may not be transmitted. (Egerton and Gates, Lafitte. (l. c.)

Campbell and Woodhead[11] have specially studied the compression waves accompanying detonative combustion. Since increase of pressure favours the setting up of a detonative type of combustion, it is possible that the rate of rise of pressure in an engine cylinder may be sufficiently great to cause a small portion of the charge to burn at the enhanced rate of a detonating type of combustion, but a true detonation wave is not set up. Maxwell and Wheeler[12] have shown photographically that enhanced combustion occurs in the neighbourhood of the walls in a cylindrical bomb when the explosion is audible, and that a shock wave can be seen to travel back through the gases enhancing their luminosity and apparently completing the combustion almost instantaneously throughout the cylinder. In non-audible explosions such as those of benzene and air there is no delay in the completion of the combustion reactions, but they are continuous and long continued behind the flame front (*cf.* [12]). The effect of reduction in the length of the cylinder, turbulence and shape of combustion space have also been investigated. It may be mentioned here that these authors found that lead tetraethyl prevented the disturbance and the production of the shock wave, only when it was previously decomposed and partially oxidised as a smoke.

In connection with these experiments reference may be made to the work of Duchène,[14] who has photographed flame travel in glass tubes connected with a cylinder in which benzene/air and cyclohexane/air mixtures were compressed and ignited by a spark. In both cases rate of flame travel increases until at a certain point a check occurs, and then proceeds fairly uniformly at a slower rate. With benzene the intensity of luminosity is uniform, but with cyclohexane the luminosity becomes enhanced in a discontinuous manner both in the burnt and unburnt gases, as if the combustion occurred in two distinct phases. The addition of lead tetraethyl inhibits the appearance of the second phase.

Lovell Coleman and Boyd[20] have recorded the composition of the gases during the progress of combustion within the cylinder by means of a sampling valve. They find that the rate of combustion is accelerated by a knocking type of explosion and delayed by an "anti-knock." Their work also indicates that combustion continues for a time after the flame has travelled throughout the charge.

Brown and Watkins[15] provide evidence that rate of rise of pressure is the dominant factor that determines the tendency of a fuel to initiate the detonation wave, but that the relative tendency to detonate may be different from the tendency to "knock" in an engine. They state that the self-igniting temperature is an important factor as well as the rate of rise of pressure. The above discussion is sufficient to draw a distinction between "detonation" as applied to the combustion of gaseous mixtures (and explosives) and as used in connection with an abnormal type of explosion in the internal combustion engine, which is perhaps better described as "knocking."

Enhanced combustion in a portion of a burning mixture is characteristic of the vibratory type of combustion which comes intermediate between real detonation and slow uniform propagation of flame. Morgan[14] has demonstrated that audibility of explosion depends on the dimensions of the containing cylinder and on the nature of the mixture. He considers that a certain rate of heat generation and a certain characteristic frequency are together necessary to provide the fluctuations required to set up violent vibrations in the burning charge. Egerton and Gates (l. c.) and Maxwell and Wheeler's (l.c.) photographs show evidence of vibrations in the burning gases associated with a knocking type of explosion. The vibratory character of the combustion of certain mixtures is further illustrated by the work of Bone, Fraser and Witt.[17] It has also to be remembered that the shape of the vessel[18] and conditions of experiment (open or closed vessel) influence the character of an explosion.

In the engine the mixture is in a state of turbulence, but that does not necessarily render the rate of flame travel uniform. Its beneficent effect has been ascribed to the prevention of gas films at the cylinder walls which cause irregular and incomplete combustion.[19] The influence of shape of head on the rate of flame travel has been investigated by Ricardo[5] by means of stroboscopic observations through quartz windows.

He[19] has also investigated the effect of position of valves and of sparking plug on "knocking"; the relation of mechanical design to "detonation" is reviewed in a recent paper.[20] "Knocking" is influenced by (1) length of flame travel (to furthest point in

combustion chamber from spark); (2) by the surface temperature of the combustion chamber (*e.g.*, by the hot exhaust valves and any circumstances which give rise to high local temperatures which turbulence tends to minimise); (3) by the temperature and density of the charge at the time of ignition.

"Knocking" undoubtedly tends to take place towards the end of the flame travel in the neighbourhood of the walls, and is assisted by any circumstances which tend to increase locally the rate of rise of pressure and of temperature (*e.g.*, ridges in the neighbourhood of exhaust valves[21] etc.); it is further influenced by the temperature and oxidation to which the unburnt charge is exposed during the compression stroke and during the travel of the flame. Any tendency to provide regions in a particularly high energy state is likely to lead to enhanced local combustion and hence to a knocking type of explosion.[22]

Tizard (l. c.) considered that "knocking" depended primarily on the rate of burning of that portion of the charge first ignited and that such rate would increase very rapidly with slight increase of flame temperature, consequently the proportion of diluent gas (exhaust gas, etc.) by increasing the specific heat in the charge and reducing flame temperature would greatly influence "knocking," as has been shown to be the case.[24] Ricardo[19] discusses Tizard's conclusions, and shows that although compression pressure appears to determine tendency to knock, it is also largely a measure of the proportion of inert diluent in the cylinder, and so affects the maximum flame temperature. These considerations are no doubt in the main correct, but there is the further influence of preliminary changes in the heated charge and the production of reaction centres. The nature of these preliminary changes, whether peroxides accumulate in the charge, etc., has been the subject of recent investigations by Callendar and associates,[23] and by Egerton and Gates.[24]

The earlier papers of Ricardo[1] and of Tizard and Pye[4] give information as to the relative behaviour of various fuels, and its relation to the ignition temperature. The tendency of a fuel to detonate is also evinced by its self-igniting temperature as measured in an apparatus such as devised by Moore.[25] Here the temperature of ignition is largely influenced by the walls of the ignition vessel, by the inert gases present and other factors.[24] But these conditions also prevail in an engine during the compression stroke, and so the tendency to ignite under those conditions gives to some extent a measure of the tendency to ignite in front of the zone of combustion in the engine cylinder. Such factors as time, pressure, etc., however, are quite different.

A flame possesses ahead of it a narrow zone in which the gases are being heated. The more readily they can ignite the quicker is

the flame propagation and the more rapid the rate of rise of pressure. Under certain circumstances there is photographic evidence for autoignition to occur in a region of high pressure (due to compression waves) well ahead of the flame.[26,27] This spontaneous ignition is of the same nature as that produced by mechanical adiabatic compression which Dixon has shown to develop gradually even in detonating mixtures.[26]

There is no evidence that spontaneous ignition of the charge well ahead of the flame front is essential to the phenomena of "knocking." Spontaneous ignition in front of the flame in the heating zone is another way of stating that the combustion becomes enchanced owing to rapid rise of pressure and temperature. Simultaneous ignition of a small portion of the charge may occur, but the mixtures are insufficiently "strong" and insufficiently homogeneous to maintain the velocity of reaction necessary to transmit the flame at the rate of the detonation wave, on the other hand a compression or shock wave is probably set up by this enhanced vibratory combustion which occurs in the neighbourhood of the walls at the end of the travel of the flame in regions of high local pressure and high reactivity.

The self-ignition temperatures of the paraffin hydrocarbons go hand in hand with their tendency to knock; aromatic substances have much higher igniting temperatures and less tendency to knock, the naphthenes are intermediate. Callendar[28] has pointed out that the tendency to detonate is the greater the higher the critical temperature of the fuel and has connected these properties with the tendency of the fuel to remain as small liquid droplets or molecular aggregates. Fuel mixtures containing liquid particles have been shown by Callendar and his associates[28], by Egerton and Gates[24], and by Aubert, Pignot and Villey[29] to ignite more readily than completely vaporised mixtures. There are no doubt many aspects of the knocking behaviour of the engine charge which can be connected with the wetness of the mixture and the presence of liquid nuclei, but there is also no doubt that completely vaporised fuel and gaseous fuels such as hydrogen can also exhibit the phenomena.

In such cases advocates of the theory would no doubt say that easily condensed products of reaction (*e.g.*, peroxides), carbon nuclei, etc., provide the necessary centres for spontaneous ignition. This more general view of nuclei gradually merges into that of the provision of reaction centres.[22]

The view that combustion of liquid nuclei essentially cause knocking has been criticised by Midgley[30], by Whatmough[21] and others.[24] The indirect evidence, as found by Egerton[31], may here be mentioned, that the rate of combustion of gaseous mixtures of carbon monoxide and air or of methane and air can be inhibited

by the same anti-knocks (*e.g.*, iron carbonyl) as inhibit the knocking combustion of the charge in an engine, may be cited in this connection. Similar influence on Inflammation limits of hydrogen/air mixtures have been found by Tanaka and Nagai[32].

Fenning[34] determined the rate of pressure rise in closed cylindrical bombs in mixtures of CO/air, methane/air, hexane/air, benzine/air and petrol/air under conditions of high initial pressure and various initial temperatures. In the case of benzene, the rate of rise of pressure and the audibility was less when the initial temperature was raised, whereas in the case of paraffin hydrocarbons the reverse was the case. These differences may perhaps be connected with the influence of slow reactions on the subsequent behaviour of the combustion.

The results of Fenning have an important bearing on the influence of temperature and diluent gases on the phenomena of knocking.

(*b*) "Anti-knocks."

Midgley and Boyd[2] gave figures for the relative effectiveness as anti-knocks of various organometallic derivatives and also of various organic nitrogen compounds; they also investigated "pro-knocks" such as amylnitrite. Figures are also available in the reports of Church, Mack and Boord[35], Callendar, King and Sims[28], Sims and Mardles[36], and of Egerton and Gates[24]. Tests carried out with different engines may give different results, depending on the temperature and other factors relating to the engine, and on the nature of the fuel to which the anti-knock is added. The above tests have either been carried out with the Delco engine fitted with bouncing pin or with the Ricardo variable compression engine. In the former case comparison is usually made against a fuel containing a known amount of "ethyl fluid"; in the latter, against a fuel containing a definite quantity of toluene[1]. Edgar[34a, 34b] has suggested the use of mixtures of 40 to 60 parts of n.heptane and 60 to 40 of isooctane, both of which can be obtained pure, as standard fuels against which to compare the "knocking" propensities of other hydrocarbon fuels[34c,d,e]. Lead tetraethyl is contained in "ethyl fluid" (55 per cent. lead tetraethyl, 36.5 per cent. ethylene dibromide, 9 per cent. monochlornaphthalene and Sudan Red), which added to petrol is sold as standard "ethyl petrol." "Iron carbonyl"[38] has been marketed as "Motyl" (mixed with paraffin hydrocarbon "dapolin"); although very effective as an anti-knock, it has disadvantages in leaving deposit of oxide on the sparking plugs and valve stems. "Nickel Carbonyl" is also effective, but is more sensitive to moisture.[37]

Sims and Mardles[36] showed that metal organosols of lead, nickel, iron, etc., showed anti-knock properties in relation to their content

of metal. They also tested metallic naphthyl, xylyl and phenyl compounds and also oleates; Church, Mack and Boord[35] also tested a number of such compounds, finding certain bismuth and cadmium compounds effective. Olin, Rhead and Goos[39] were not successful in suppressing detonation with nickel in colloidal suspension, but there seems no doubt that if the metal is in a sufficiently fine state of division, it can be effective. Egerton and Gates[24] showed that the effect of vapours of metal on the igniting temperatures of petrol were of the same order of effectiveness as that of the organometallic anti-knocks dissolved in petrol. By an arc arrangement they were able to vaporise metals and find out which were effective —amongst the most effective being thallium and potassium. Bismuth and manganese were also found effective. (It is mentioned in the paper that Ricardo and Thornycroft confirmed the anti-knock behaviour of lead and of thalliuin vapour from an arc arrangement attached to the induction pipe of an engine.) That the metal atom obtained by dissociation of the organometallic molecule is the effective constituent is further confirmed by the work of Church, Mack and Boord[35] who state that lead triethylchloride is three-fourths and lead diethyldichloride one-half as effective as lead tetraethyl. These compounds in dissociating no doubt do not give free lead atoms but lead chloride molecules. It is argued by Egerton and Gates[24 32] (from the behaviour of potassium, etc.) that the metal atom must be in an incipient state of oxidation, that those metals only are effective that can be taken from a higher to a lower state of oxidation and then reoxidised and that the oxide must be in a vapour state, *i.e.*, must not form conglomerated particles. Callendar[23] on the other hand considers that the organometallic substance is concentrated on the surface of the droplets, dissociates and protects the droplet from oxidation and self ignition by its reducing action on the peroxides. Moureu and Dufraisse[40] also consider that the anti-knock delays oxidation in the liquid droplets or nuclei, but by the same action as "antoxygenes" delay the "autoxidation" of liquid organic substances (*e.g.*, oxidation of aldehydes inhibited by phenols[41]).

Callendar and associates[23], Egerton and Gates[24], have shown that anti-knocks act as inhibitors of oxidation and not as multiple ignition centres as suggested by Church, Mack and Boord[35]. They have shown that they inhibit oxidation during the compression stroke in the engine (*cf.* Dumanois[41a] who also comes to a similar conclusion). Although the metal atom is mainly influential in the inhibition, the organic groups with which it is associated modify to some extent its behaviour (thus lead phenyl is less effective than lead ethyl). Much work has been done on the behaviour

of organic anti-knocks, such as aniline or xylidine. Callendar[23] showed that in most cases these had high critical temperatures and would become concentrated in droplets and delay their oxidation. Egerton and Gates[24] investigated the effect of such substances on igniting temperature and concluded that their action was similar to that of the organometallic anti-knocks, only as they themselves undergo combustion that larger quantities were needed. It was found that quinone, a product of the oxidation of aniline[41b], was nearly as effective as aniline. Callendar[23] found phenol also effective. Many organic nitrogen, some iodo, and some sulphur compounds are amongst the effective organic compounds.

Weerman[42] first showed that the self-igniting temperature of petrol was raised by an anti-knock, but this only occurs with air, not in oxygen; in the case of the alcohols, Tanaka and Nagai[43] found the reverse was the case. Egerton and Gates[24] extended such studies and investigated the effect of concentration of hydrocarbon, of mixtures with acetaldehyde, with ether, carbon disulphide, etc. They showed that the anti-knock particularly inhibits the ignition of aldehydes. Callendar and Mardles[23], Lewis[44], and Mardles[45] have investigated the effect of anti-knocks on the temperature at which combustion sets in, and have found—besides aldehydes, CO_2, water, etc.—that peroxides are formed rapidly in these preliminary stages, particularly in a system of liquid droplets. Callendar considers that "the peroxide, accumulating in the droplet, acts as a primer causing simultaneous ignition of the droplets." Egerton[32] has put forward the view that, prior to ignition, reaction occurs through a chain mechanism, that a temporary peroxide may be formed as a primary product of oxidation and that the active products of its reorganisation or decomposition propagate the chain. The effect of concentration on the transmission of the chain is important and serves to assist oxidation at the surface of a droplet. The anti-knocks are considered as chain breakers. This action, together with their regeneration by further oxidation, is sufficient to account for the small quantities required. Lewis[44] upholds that the fuel first undergoes a certain degree of dehydrogenation, and that the hydrogen thereby becomes free to be oxidised, while the lead tetraethyl inhibits such attack. The view seems not in accord with the hydroxylation theory of Bone[46] which in its main consequences is well supported by experiment. Mardles[46] shows that unstable peroxides are formed in the preliminary stages of reaction when combustion commences, in the case of hydrocarbons but not in the case of alcohols. Aniline is stated to be more oxidised in presence of hexane than alone at the same temperature. The primary higher oxides formed in the fuel are considered as being reduced by the metal of an organo-

metallic anti-knock, but it is noteworthy that metals which are highly reducing are not necessarily most effective, nor is the fact that so small quantity is required sufficiently accounted for.

The anti-knocks are found to lower the temperature at which oxidation becomes noticeable. Callendar[23] has investigated the addition of aldehydes, peroxides, etc., on the H.U.C.R., and compared the effect with that of the pro-knock amylnitrite. Brunner and Rideal[47] have investigated the oxidation of the vapour of n. hexane and have found that there is a period of induction during which some catalyst, probably produced at the walls, accumulates, so that there is no definite temperature of initial combustion. He likens the case to that of the autoxidation of benzaldehyde to perbenzoic acid which, according to Reiff[49] and to Brunner[50] is initially a surface reaction but subsequently becomes homogeneous, when the concentration of autocatalyst becomes sufficient. The period of induction is affected by inhibitors.

Hinshelwoods'[48] work on the homogeneous combination of hydrogen and oxygen below the igniting temperature and his interpretation of the results as a chain reaction phenomenon has a close bearing on these questions. He finds the surface of the vessel in which the reaction occurs stops the chain and that inert gas has a shielding effect in inverse proportion to the diffusivity. Inhibitors seem to act throughout the gas very much as the walls of the vessel do, as pointed out by Egerton and Gates[24] in considering ignition. It was also considered that ignition of a combustible mixture in a closed space depends on the setting up of centres of high energy. Pease and Cheseboro'[51] also discuss the effect of surface in preventing the reaction of hydrogen and oxygen and put forward similar considerations.

Some active atoms may lose their energy as luminous radiation and chemiluminescence may accompany these reactions. Conversely illumination may influence the rate of reaction; Bennett[52] found that the temperature of initial combustion was influenced by the light of the mercury arc. The close connection between the chain reaction mechanism in the photochemical oxidation of benzaldehyde and its thermal oxidation in the liquid state has been pointed out by Bäckstrom[53]; the significance of these reactions in many oxidative reactions he has also discussed, particularly the oxidation of phosphorus. Semenoff[54] has further investigated this reaction and has shown how the reaction chains by branching can lead to explosive combustion. It is noteworthy that fluorescent power is also inhibited by the same substances as delay oxidation and acts as anti-knocks, the question of the interchange of energy between the same and different kinds of molecules being here brought into prominence.[55] The initial[32]

stages of the combustion process are of great importance in the interpretation of the inhibition caused by "anti-knocks."

Egerton[31] has shown that the rate of combustion of a completely gaseous system such as CO/air is modified by very small quantities of iron carbonyl, although it is unaffected by lead tetraethyl. It is essential that the organo-metallic inhibitor should be decomposed and rendered active within the narrow zone of combustion in order that it should become effective. Lead ethyl has been found to affect the rate of slow pentane flames.[6] The reason for the lack of effect of anti-knocks in delaying detonation in a tube or in appreciably affecting adiabatic ignition temperature[29] is that in such explosions there is so much heat available that the reactions have been autoaccelerated before they can be affected by the inhibitor. That is not the case in the engine cylinder.[32] Tanaka and Nagia[56] have investigated the effect of diethylselenide, hydrogen selenide, tin tetramethyl and lead tetramethyl, etc., on the limits of inflammation of hydrogen/air and hydrocarbon/air mixtures. The lower limits are reduced but the upper limits are decreased at first and then may increase again. Tanaka considers that the flame temperature of the combustible is too low and so it loses activation energy to the inhibitor until the latter is itself sufficiently activated to burn, when the whole mixture will burn at the higher flame temperature corresponding to that at which flame can be propagated in the inhibitor. The subsequent rise in the upper limit is considered to be due to heat liberated by combustion of the inhibitor, when the quantity becomes considerable.

There have been several theories advanced to explain the behaviour of anti-knocks based on ionisation or radiation effects.[59] For instance, it was suggested that electrons, which projected from the burning gases, precede and engender the flame, would be collected by the positively charged metal atoms of the anti-knock and so reduce the rate of flame propagation. Apart from the lack of evidence of such a cause of flame propagation, the effect of anti-knocks on ionisation in flames and in the preflame period has not been found in agreement with the suggestion. Wendt and Grimm[57] obtained a positive result for the effect of lead ethyl on the rate of decomposition of ions in benzene/air mixtures but Clark and Thee[58] failed to confirm it using a more constant source of ionisation.

Garner and Saunders[60] gave a general account of the connection between ionisation as caused by thermal and chemical changes, referring to the work of Brewer,[62] Lind and others.[64] Although ionisation through chemical change occurs as well as thermal ionisation, yet the number of ions produced and the relation of ignition temperature are not such as would point to ionisation

being a process necessarily preceding combustion. Garner and Saunders found that knock inducers on the whole increase ionisation in flames of hydrogen and oxygen, and anti-knocks decrease it, probably because of the effect on the temperature of the flame, the velocity, however, was not found to be appreciably affected. Further studies have been made by Saunders[61] on CO/O_2 Methane/O_2, and acetylene/O_2 mixtures. The maxima for ionisation on the whole agree with those calculated on the Saha theory; ionisation being mainly thermal in origin. Bennett[65] investigating ionisation in the Bunsen flames and flames of hexane, found further evidence against Wendt and Grimm's suggestion, for increased ionisation was found in presence of iron carbonyl and lead tetraethyl. He concludes ionisation does not seem to be a cause or effect of "detonation," but mainly a temperature effect.

In another paper Bennett[66] finds that the slow combustion of a disperse system of liquid drops of various organic substances in air is accompanied by liberation of electrons, whereas in the mixture of the vapour and air much fewer electrons are present at the same temperature. He considers that the supply of energy for the recombination of positively charged ions into which the drops divide may account for the easier ignition of a system containing droplets. The effect of anti-knocks and pro-knocks, however on the ionisation of mixtures of undecane, and air at low temperatures does not lead to any definite connection between ionisation and the action of anti-knocks. Bennett and Mardles[67] have further investigated the ignition of droplets of various organic liquids and find ionisation accompanies fog formation. Aldehydes and peroxides were found to be present in the liquid droplets. Ionisation is only slight at temperatures well above the temperature of initial combustion, even though production of aldehyde may be fairly extensive. Energetic reactions, such as the scission of oxygen molecules, would no doubt involve liberation of some electrons, and, consequently, ionisation. The ionisation curve for hexane/air and undecane/air mixtures treated with iron carbonyl crosses those for the untreated mixtures; "increased ionisation at higher temperatures being probably due to the increased combustion of the metallic particles produced by the thermal decomposition of the metallic compounds." A remarkable increase in ionisation was obtained for CO/H_2/air mixtures in the presence of iron carbonyl, although an iron carbonyl air mixture alone showed no such effect.

On the whole the evidence is that ionisation is an accompaniment of the chemical and thermal processes occurring and not a determining cause. It may well be that the initial stage of reaction is associated with the production of a very small number of

particularly active centres and that ionisation (involving as it does a considerable energy change within the molecule) may accompany the formation of such centres; the number, however, of ions would be exceeding small, as is evidenced by the number present during the oxidation of phosphorus.[68] The work of Finch[69] must be noted in this discussion. The latter finds inter alia that in the combustion of moist CO, if ionisation is sufficiently intense, the presence of water makes no difference to the rate of combustion of CO and oxygen.

Views have also been held as to the part played by radiation in the propagation of flame, and the effect of anti-knocks in absorbing such radiating and so delaying combustion. Garner[70] has shown that the infra-red radiation is greatly increased in the combustion of CO/air mixtures when they are dry and, consequently, slower burning. The proportion of energy which is radiated in such a chemical change may thus modify considerably the rate of the reaction. Carbon tetrachloride behaves as a negative catalyst and decreases the speed of the flame and increases the radiation emitted. Nitrogen peroxide has been found to behave as a feebly positive catalyst in dry mixtures, but as a negative catalyst in imperfectly dried mixtures. These experiments have an important bearing on the mechanism of combustion. The ultra-violet radiation emitted in a detonating explosion and also in explosion of a knocking character extends further than in a normal combustion, as the experiments of Clark and Thee[71] and Clark and Henne[71] have shown. But there is no evidence that the effect is other than an accompaniment of the higher temperatures produced, neither is there any evidence of the absorption of such radiation by the anti-knock being instrumental in the prevention of activation of the combustible gas ahead of a flame. Many substances absorbing such radiation are much less effective in preventing the spread of flame than those which do not absorb.

A considerable literature has grown up respecting the toxic properties of "anti-knocks," their methods of manufacture, their suitability for and comparison in various types of engines, their effect on various parts of the engine (nature of deposits, etc.), but these matters are not within the province of this review.

For general information on work that has been carried out on anti-knocks see references 1, 28, 23, 32, 21, 72, 73, 74 and 75.

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Developments of Petroleum and Natural Gas in Canada.*

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Petroleum is produced in Canada in three Provinces—namely, New Brunswick, Ontario and Alberta. Natural gas supplies also occur in these same three provinces and a small amount is being

* Published with the permission of the Director, Geological Survey of Canada, Ottawa. Paper received May 21, 1928.

produced in Manitoba. The production and value for the last three years are as follows :—[1]

PETROLEUM.

	1925.		1926.		1927.	
	Barrels.	Value $.	Barrels.	Value $.	Barrels.	Value $.
New Brunswick .	5,376	16,805	10,544	29,940	18,244	41,748
Ontario ..	143,445	390,410	137,850	379,221	140,105	289,390
Alberta	169,432	758,837	216,050	902,504	321,154	1,189,007
Total ..	318,253	1,166,052	364,444	1,311,665	479,503	1,520,145

NATURAL GAS.

	1925.		1926.		1927.	
	M. cu. ft.	Value $.	M. cu. ft.	Value $.	M. cu. ft.	Value $.
New Brunswick .	639,235	122,394	648,316	128,300	630,755	124,637
Ontario ..	7,040,564	3,888,400	7,764,996	4,409,593	6,965,117	4,027,479
Manitoba ..	200	60	200	60	200	60
Alberta	8,998,931	2,700,025	10,794,697	3,019,221	12,933,801	3,589,485
Total ..	16,678,930	6,710,879	19,208,209	7,557,174	20,529,873	7,741,661

MARITIME PROVINCES.

In New Brunswick the total production of both petroleum and natural gas comes from the Stony Creek field. The increase in petroleum production, which in 1927 was more than three times that of 1925, is mainly due to a more vigorous policy of development of the oil resources of this field. Natural gas from this field has been supplied to Moncton and adjoining towns for many years.

Considerable activity in exploration for petroleum and natural gas was manifested in the Maritime Provinces in 1927. In Cumberland Co., N.S., near Nappan, the Imperial Oil, Ltd., drilled a number of shallow holes to determine the geological structure. No deep drilling has been attempted and no results from the exploratory work are yet available. A similar programme of shallow drilling for the determination of structure has been done near Mabou and Margaree, in Inverness Co., Cape Breton, by the Eastern Gulf Company. It is not known what results have been achieved.

On Prince Edward Island the H. L. Doherty Company drilled a deep test for oil. The well was abandoned at a depth of approximately 6,000 ft. without any natural gas or oil being discovered. The strata penetrated by the well were red and grey sandstones and shales, and are thought to be fresh-water sediments of Upper Pennsylvanian or Permian age.

ONTARIO.[2]

Drilling in Ontario in 1927 was mainly done by the gas companies in order to maintain as large a gas supply as possible. The Union

[1] Dominion Bureau of Statistics.

[2] Information supplied by R. B. Harkness, Natural Gas Commissioner for Ontario.

Gas Company and Southern Ontario Gas Company have shot all wells in the Tilbury field in Kent Co., using about 250 lbs. of dynamite in each well. The gas in the Tilbury field comes from the Onondago (Devonian) limestone, and it is understood the shooting of the wells has provided an enormous increase in the open flow of the wells.

In Romney Township, Kent Co., the Southern Ontario Gas Company has recently completed a well with an open flow of approximately 3 million cu. ft. per day. This is much the largest well completed in recent years.

There has been a small increase in oil production in 1927 over 1926, but it is understood this is not due to any new important discoveries.

MANITOBA.

In Manitoba[3] there has been a small natural gas production for many years from shallow wells drilled in Cretaceous shales. At Treherne, about seventy miles south-west of Winnipeg, gas from one well has been used by a farmer for fifteen years mainly for lighting purposes, the supply not being sufficient for heating. In the Rothwell area, east of Treherne, another well has been used for lighting for six years. In both cases the depth of the wells is less than 200 ft. In the south-western part of Manitoba, south-west of the town of Deloraine, there are four wells in active use in and near the town of Waskada, but the supply from the wells is small and is sufficient only for lighting and cooking purposes for the owners. Another well, drilled in 1926, about twenty miles north-east of Deloraine, found gas at 190 to 210 ft. in depth. The closed pressure of the well amounted to 45 lbs. In general the supply from these shallow wells would not be expected to be large, and as yet no large fields have been discovered.

ALBERTA.

The recent activity in petroleum exploration in Alberta dates from the autumn of 1924, when Royalite No. 4 well, in Turner Valley, thirty-five miles south-west of Calgary, came in with a gas flow of 17 to 20 million cu. ft. per day. High grade naphtha of 72° to 73° Baumé is extracted from this gas by using two Smith separators, and the gas which is treated in a scrubbing plant in Turner Valley is now piped to Calgary for domestic and industrial purposes. Due to the production of Royalite No. 4 well, the

[3] Information from Wallace, R. C., and Greer, L. The non-metallic Mineral Resources of Manitoba. Industrial Development Board of Manitoba, 1927.

production in Alberta increased from 844 barrels in 1924 to more than 169,000 barrels in 1925. Since that time the flow of Royalite No. 4 well has continued without diminution of volume, but with an increase in naphtha content, until at the present time production is 600 to 650 barrels per day. This production was secured in Royalite No. 4 well at a depth of 3,740 ft. from a zone of porosity in the upper part of the Palæozoic limestones and dolomites. Regional studies which have been made by the geological survey and by other geologists interested in petroleum development have shown that the Upper Palæozoic in this part of the Foothills is presumably Pennsylvanian in age and is overlain conformably by the Fernie formation of Jurassic age, although in the Banff area, only seventy miles to the north-west but in the mountains, there are approximately 3,400 ft. of Triassic and a considerable thickness of strata either of later Pennsylvanian or Permian age.

The results of Royalite No. 4 well stimulated activity in Turner Valley, and during 1925 a number of wells were started but none were completed until 1926, when three wells—Illinois Alberta No. 1, McLeod No. 2 and Vulcan No. 1—obtained production in approximately the same horizon as Royalite No. 4 well. A geological study of Turner Valley in connection with a study of data from well borings has demonstrated the fact that Turner Valley is a double-crested anticline with a very deep, sharply-folded and somewhat faulted central syncline. Royalite No. 4 well is on the eastern anticline of this double-crested fold, whereas Illinois Alberta No. 1 and McLeod No. 2 are on the western anticline. Vulcan No. 1 well is in the central syncline and obtained production in the top of the Palæozoic rocks at a depth of slightly more than 5,000 ft. The top of the Palæozoic limestone in Vulcan No. 1 well is more than 1,400 ft. deeper than in Royalite No. 4 well, and it is very significant that even at this depth oil and gas have been encountered and water is absent. The results obtained by drilling in 1926 justified the assumption that the porous zone of the Palæozoic was of wide extent under Turner Valley, and it was, therefore, anticipated that other wells, which were properly located with regard to structure, would doubtless find production in the same zone. This assumption has been wholly justified by the drilling campaign of 1927 and early months of 1928, and four other wells have now (March 31) been completed and have obtained production in the Palæozoic horizon. It is a fact worthy of notice that no well drilled within Turner Valley to the Palæozoic horizon has been a dry hole, nor has any well found any water in this deep horizon. Vulcan No. 1 Well is the deepest (5,004 ft.) that has reached production in the Palæozoic rocks, and from this it might be inferred that all wells on the flanks that reach the Palæozoic at a depth not

greater than this should achieve production, but the limits of production on the flanks are not known. It appears, however, that the folds are symmetrical with their axial planes dipping steeply west. For this reason steeper dips occur on the east flank than on the west, and hence it is thought the field is likely to be narrower to the east of the axis of the eastern anticline than it will be to the west of the axis of the western anticline.

Other than the production from the lower Palæozoic zone, the most interesting development in 1927 was the finding of petroleum-bearing horizons in Home No. 1 and Dalhousie No. 5 Wells in the southern part of Turner Valley. The age of the producing horizon in Home No. 1 well is considered to be Lower Cretaceous at the base of the Kootenay formation, and is yielding oil of 44° A.P.I. Dalhousie No. 5 Well produced[4] slightly more than 60 barrels per day of 50° A.P.I. crude oil during February, 1928, from a sand in the Fernie (Jurassic) formation. Besides these productive zones there are several wells in Turner Valley producing from other Lower Cretaceous horizons, the oil being a high grade crude of 50 to 55° Baumé. The production from Turner Valley oil field for the month of February, 1928, was as follows :[5]

Crude Oil.			
McLeod No. 3. Dalhousie No. 5. Home No. 1. Royalite No. 10 Okalta No. 2. McDougall-Legur No. 1 " " No. 2 Dalhousie No. 6.	5,600 barrels.		
Naptha.			
Royalite No. 4 ..	18,387 barrels.	Average	636 per day.
Royalite No. 7 ..	3,076 "	"	106 "
McLeod Illinois-Alberta Vulcan	4,485 "	"	154 "
Casing.			
Royalite No. 1 and 2	40 barrels.		
Total	31,588 barrels.		

The price paid for the naphtha is $3·95 per barrel at Turner Valley.

The decidedly favourable results of drilling in Turner Valley have focused the attention of oil operators on the Foothills belt, and much geological work is being done in the effort to locate other folds suitable for oil accumulation. Several wells are being drilled in various parts of the Foothills and on the adjoining plains, but only one of these was completed in 1927. This was the Imperial Oil (Ltd.) Well in the Jumping pound area south of the Bow River and almost directly west of Calgary. The well passed through

[4] Communication from Dr. O. B. Hopkins, Imperial Oil, Ltd.

[5] *Bull. Can. Inst. Min. and Met.*, April, 1928. p. 451.

what is thought to be a thrust fault and was abandoned at a depth in excess of 5,000 ft. Several of the wells now drilling should be completed in 1928.

From results obtained in Turner Valley it is known there are at least four zones in which production may be encountered. These consist of two zones thought to be in the Lower Cretaceous, one of which is near the top and the other at the base; one horizon in the Jurassic and one zone in the top of the Palæozoic limestones and dolomites. Sufficient data is not yet available to form any opinion in regard to the extent these zones may be expected to yield oil in the Foothills belt outside of Turner Valley, but such evidence as is at hand indicates that the horizons in the upper part of the Lower Cretaceous are persistently oil-bearing. The evidence in regard to the prospects of production from the zone in the upper part of the Palæozoic limestones and dolomites is fairly conclusive. An examination by the Geological Survey of the upper part of the Palæozoic in the Moose Mountain area, twenty-five miles north-west of Turner Valley, showed at least 30 ft. of strata in several zones, with a high degree of porosity and containing a bitumen-like residue such as would be expected to be left after dissipation of a former petroleum content. From geologists engaged in commercial work it has been learned that this same condition is to be found in the Palæozoic rocks, where they outcrop on the eastern-edge of the mountains on Red Deer River, eighty-five miles north west of Turner Valley. These occurrences of porosity, with evidences of petroleum, lead to the assumption that this zone of porosity is of very wide extent in an area north-west of Turner Valley. To the south-east of Turner Valley the Geological Survey has made no investigations of the extent of this porous zone although it is said to be present. The presence of this porous zone over a wide area in the Foothills is regarded as being highly significant since this zone has proven to be so prolific of production in Turner Valley.

The most important developments on the Plains in 1927 was the securing of production in the Devenish Well in Southern Alberta, in the Skiff area, east of Lethbridge. The oil[6], which is about 19° Baumé, was encountered in Jurassic strata at a depth of approximately 3,080 ft. The well was reported to have flowed, but the amount of production is not known as no continuous test had been made up to the end of the year 1927. The Devenish Well is on the structure known as the Bow Island anticline, which in an east-west direction is a very broad arch, but slopes from the area of the Sweetgrass uplift in Montana, northward into Alberta. It is known that there are several minor folds on this major structure, and it is possible the Devenish Well may be on one of these, although the

[6] *Bull. Can. Inst. Min. and Met.*, Sept., 1927, p. 994.

Geological Survey at present has no detailed information. It is reported that arrangements have been completed for further tests of this area during 1928.

In North Central Alberta the most important development of 1927 was the bringing in of the National Exploration Company's well in the Wainwright field at a depth of 2,237 ft., with a heavy gas flow which measured 14,000,000 cu. ft. Later, however, the gas flow diminished somewhat in volume and oil shows were reported.[7] The depth at which this gas flow was encountered suggests that the horizon which is producing it is the horizon that is giving oil production in a number of other wells in the Wainwright field, and hence, if the gas and oil are in the same horizon, the prospects for larger oil wells than have hitherto been obtained would seem to be good. There is a possibility, however, that the oil and gas horizons are separated by a thin amount of shale—a condition suggested by the character of the oil sand encountered in the producing oil wells and by the fact that the volume of gas from producing oil wells in this field is relatively small in comparison with the amount obtained in the National Exploration Well.

East of the Wainwright field in the Ribstone area, in the vicinity of the Alberta-Saskatchewan boundary, where a structure favourable for oil accumulation was outlined by the Geological Survey in 1925, there have been two tests drilled. The first of these drilled by the Imperial Oil, Ltd., in 1926 gave a flow of gas reported to be 3,000,000 to 4,000,000 cu. ft. per day at a depth of 1392 ft. and an oil sand was encountered between 1870 to 1900 ft. This gave only three to four barrels of oil per day. The well was drilled to a depth of 3489 ft. and was abandoned after having penetrated the Devonian to a very considerable depth. Ribstone Oils No. 1 Well, six miles north-east of the Imperial Well, encountered a show of oil and a large amount of water at the same horizon that was tested for oil in the Imperial Well. The well is being deepened, but other tests will be made. Ribstone Oils, Ltd., have drilled more than twenty-five shallow holes to determine the structure which on account of the glacial cover could be outlined only in a very general way from the limited number of rock outcrops in this area. The shallow drilling has proven that the structure is even more favourable than originally thought, and it is now known Ribstone Oils No. 1 Well was an edge location and much more favourable drilling sites can be chosen. The new tests proposed for 1928 should therefore give conclusive results concerning the oil prospects of this area.

Drilling for natural gas in Alberta in 1927 was on a small scale owing to the large amount of gas now available from Turner Valley. Two wells, one with an open flow of 8,000,000 and the other with

[7] *Bull. Can. Inst. Min. and Met.*, Sept., 1927, p. 995.

5,000,000 cu. ft. per day were drilled in the Viking field from which supplies of gas are piped to Edmonton and adjoining towns. In the Foremost field in Southern Alberta one well was drilled but failed to give commercial production. In the Medicine Hat gas field two deep tests for oil have been made. Both of these obtained gas in the Medicine Hat gas sand, but got no further production at depth. Both have been abandoned as far as deep production is concerned, but the gas from the Medicine Hat gas sand will be utilised to augment the supply from other wells. In No. 2 Well, drilled in 1927, the gas in the Medicine Hat sand was encountered between 1252 and 1270, and the open flow was approximately 2,500,000 cu. ft. per day.

The results of drilling in Alberta during 1927 have been very encouraging for further exploration, and it is anticipated that there will be a large increase in oil production in 1928.

British West Indies.*

By A. P. CATHERALL, B.Sc., M.I.Min.E., A.M.Inst.M.M. (Member).

TRINIDAD.

NOTWITHSTANDING the general depression existing in the oil industry during a considerable part of the past year, it is pleasing to be able to record that there has been an increase in the development of the oil industry of Trinidad during the period under review. The greater part of the production of the Colony is still obtained from the Fyzabad-Morne L'Enfer-La Brea districts, from which an increasing production has been obtained.

Intensive development was continued in the Palo Seco-Erin and Guayaguayare districts, though towards the close of the year steps were taken to curtail drilling operations in the latter district. In neither of these areas have large productions been obtained.

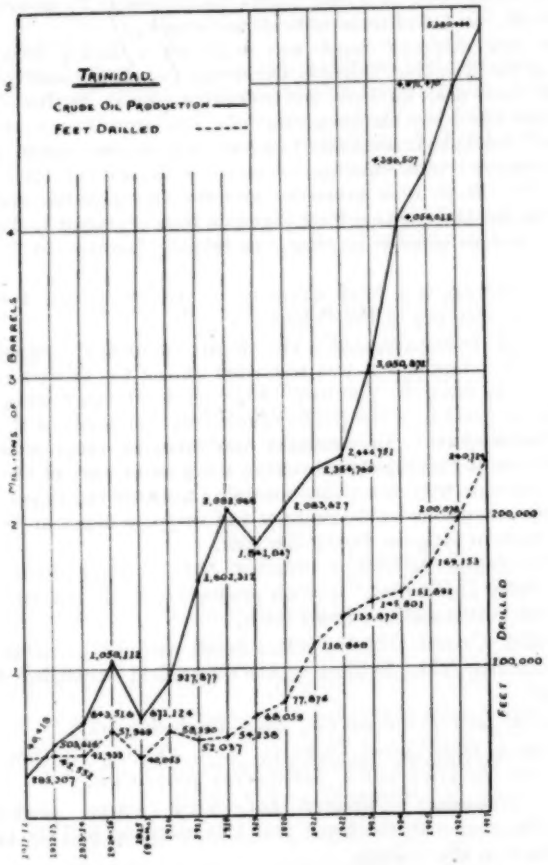
Both the footage drilled and the quantity of oil produced during 1927 showed a considerable increase over the previous year, as will be shown from the following table :—

	Year ended December 31, 1925.		Year ended December 31, 1926.		Year ended December 31, 1927.	
	Feet drilled.	Oil won. Barrels of 35 gals.	Feet drilled.	Oil won. Barrels of 35 gals.	Feet drilled.	Oil won. Barrels of 35 gals.
Crown lands	105,631	2,877,437	126,339	2,976,227	119,284	2,362,150
Private lands	63,522	1,509,070	73,739	1,995,243	121,440	3,018,314
	169,153	4,386,507	200,078	4,971,470	240,724	5,380,464

* Paper received May 29, 1928.

The accompanying diagrams will show these figures over the period 1911–12 to 1927.

As is only to be expected in view of the increased production, the exports of petroleum products have shown a considerable



increase as compared with previous years, the figures being 155,900,000 gallons, as against 139,500,000 gallons of oil for the year 1926. Owing to the low price of oil obtainable in the world's markets for these products during the past year, the values of the

petroleum products exported have actually decreased, the figures being £1,783,000 as against £1,871,000 for 1926.

The total number of wells drilled in the Colony to December 31. 1927, is 1,312, of which 823 are on Crown lands. During the year under review 158 new wells were drilled, of which 84 were on Crown lands and 74 on private lands—an increase of 31, as compared with 1926. In 116 of these wells oil was struck.

One new shipping depot was constructed during 1927—viz., that of the Trinidad Oilfields Operating Co., Ltd., who installed a tank farm near La Brea and erected a pier at La Brea Point, on which was laid a shipping line.

The Trinidad Leaseholds, Limited, during the whole period under review, were making extensive additions to their plant generally. Steps were taken to increase the pipe-line capacity by replacing the existing 6 in. pipe-line from Fyzabad to Point-a-Pierre, and to greatly increase the refining facilities at Point-a-Pierre.

The following is a brief summary of the operations of the oil companies working in the Colony :—

Trinidad Leaseholds, Ltd.—The most important company in the Colony. Production was restricted during the greater part of the year in order to purchase crude oil from other companies. The major portion of the production is from the fields at Fyzabad and Barrackpore. An extensive development programme was undertaken at Guayaguayare during the greater part of the year, but operations were somewhat curtailed towards the close. Considerable extensions to the refinery and shipping depot at Point-a-Pierre were in progress during the year.

United British Oilfields of Trinidad, Ltd.—Drilling was confined to the Parry Lands field. A small production is still obtained from the Point Fortin and Los Bajos fields.

Trinidad Central Oilfields, Ltd.—Small amount of drilling on the Tabaquite field. Drilling on the Cruse field suspended during the year.

Trinidad Lake Petroleum Co., Ltd.—Producing only.

Petroleum Development Company, Ltd.—Drilling on Crown oil rights near the Pitch Lake. Satisfactory production.

Apex (Trinidad) Oilfields, Ltd.—Very active programme during the year with the result that this company had the largest production in the Colony.

Kern Trinidad Oilfields, Ltd.—Development of Perseverance Estate, Guapo, continued during the whole of the year. Operations were continued on Crown lands near Guapo. A satisfactory production was obtained.

Oropouche (Trinidad) Oilfields, Ltd.—Now acquired by Trinidad Leaseholds, Ltd. Small production obtained.

Trinidad Petroleum Development Company, Ltd.—A very active development programme has been carried on in the Palo Seco district, but up to the present the production has been relatively small. Drilling has also been undertaken in the Cedros district with disappointing results.

Petroleum Options, Ltd.—The properties of this Company have now been leased to the Trinidad Oilfields Operating Co., Ltd.

Venezuelan Consolidated Oilfields, Ltd.—This Company was formerly the Trinidad Friendship Petroleum Co., Ltd. Towards the close of the year an active drilling programme was commenced with a resultant increase in production.

British Controlled Oilfields, Ltd.—Drilling operations have been suspended since January, 1926, and a very small production is obtained from existing wells.

Trinidad Oil Producing and Refining Co., Ltd.—Producing only during the early part of the year. Lease surrendered to owner as from June 28, 1927.

Palo Seco Oilfield (C. C. Stollmeyer).—Drilling continued during the period under review and a small production was obtained.

Trinidad Oilfields Operating Company, Ltd.—This Company continued a most active programme, with the result that it now has the third largest production in the Colony.

BARBADOS.

The British Union Oil Company, Limited, have continued development operations in this Colony, but so far production has not be obtained on a commercial scale.

BRITISH GUIANA.

No petroleum has yet been obtained in this Colony.

World's Production of Crude Petroleum.

By GEORGE SELL (Member).

ACCORDING to the returns and estimates at present available, the world's production of crude petroleum during 1927 amounted to 168,817,000 metric tons, an increase of about 14·7 per cent. over the total for 1926. The production of the various countries, together with the percentages of the total, are given in the table below, the figures for 1926 being included for comparison :—

WORLD'S PRODUCTION OF CRUDE PETROLEUM.

Country.	1926. Quantity. Metric Tons.	1926. Per-centage of total.	1927. Quantity. Metric Tons.	1927. Per-centage of total.
United States	102,783,200	69·843	120,773,000	71·541
Russia	8,500,000	5·776	9,570,000	5·669
Venezuela	5,420,000	3·683	9,200,000	5·450
Mexico	12,056,000	8·192	8,560,000	5·070
Persia	4,700,000	3·194	5,015,000	2·971
Rumania	3,244,000	2·204	3,661,000	2·169
Dutch East Indies ..	2,905,000	1·974	3,448,000	2·042
Colombia	864,000	0·587	1,950,000	1·155
Peru	1,500,000	1·019	1,366,000	0·809
Argentina	1,060,000	0·720	1,160,000	0·687
Poland	796,000	0·541	742,000	0·440
Japan and Formosa ..	266,000	0·181	238,000	0·141
Egypt	172,000	0·117	183,000	0·108
Germany	87,000	0·059	93,500	0·055
France	75,000	0·051	82,500	0·049
Ecuador	38,000	0·026	64,000	0·038
Czecho-Slovakia ..	10,000	0·007	15,000	0·009
Italy	6,000	0·005	7,500	0·004
British Empire:				
India	1,250,000	0·849	1,172,000	0·694
Trinidad	663,000	0·450	714,500	0·423
Sarawak	712,000	0·484	712,000	0·422
Canada	45,700	0·031	60,000	0·036
Other Countries ..	10,000	0·007	30,000	0·018
Total	147,162,900	100·000	168,817,000	100,000

The production of crude petroleum in the United States during 1927 showed an increase of about 17·5 per cent. over the previous year, the total for 1927 being 120,773,000 metric tons, or more than 70 per cent. of the total world's production.

The decrease of about 29 per cent. in the production from Mexico has brought that country to the fourth place in the world's table, its production for 1927 being exceeded by that from Venezuela.

The most notable increase in production is that of Colombia, which produced about 125 per cent. over the figure for the previous year. Other large increases are recorded from Venezuela and from Ecuador, both of which countries showed a rise of about 70 per cent. as compared with 1926.

The total production from the oilfields in the British Empire declined slightly in 1927, being 2,658,500 metric tons as compared with 2,670,700 metric tons in 1926. Expressed as percentages of the total world's production these figures represent 1·6 in 1927 and 1·8 in 1926. Canada produced about 31 per cent. more oil in 1927 than in 1926, this being due to increased activity and development in the Provinces of New Brunswick and Alberta. Trinidad also showed an increase of nearly 8 per cent. over the previous year, while India decreased slightly.